QUALITY ASSURANCE PROJECT PLAN

for the

Virginia River Input Monitoring Program

Prepared by

Kenneth E. Hyer and Douglas L. Moyer
U.S. Geological Survey
1730 E. Parham Road
Richmond, VA 23228

for
Virginia Department of Environmental Quality
Chesapeake Bay Office
PO Box 1105
Richmond, VA 23218

Effective June 15, 2011

Approvals:

_____

Kenneth E. Hyer, Project Manager, USGS Date

_____

John D. Jastram, Quality Assurance Officer, USGS Date

_____

Frederick A. Hoffman, Project Officer, VDEQ Date

_____

Quality Assurance Officer, VDEQ Date

_____

Project Officer, US EPA Date

_____

Quality Assurance Officer, US EPA Date

QUALITY ASSURANCE PROJECT PLAN

for the

Virginia River Input Monitoring Program

Prepared by:

Kenneth E. Hyer and Douglas L. Moyer

U.S. Geological Survey

for

Virginia Department of Environmental Quality

Chesapeake Bay Office

Richmond, VA

updated June, 2011

TABLE OF CONTENTS

I. PROJECT DESCRIPTION

A. Background

Quantification of the loads of nutrient and suspended solids into the Chesapeake Bay, and evaluation of the trends in constituent concentration are necessary in order to determine the effects that these constituents have on the ecosystems of the Chesapeake Bay. The Virginia River Input Monitoring Program (formerly known as the Virginia Fall Line Nutrient Input Program) was developed to quantify and assess the effectiveness of programs aimed at reducing the impact of nutrient and suspended solid inputs. Load estimates can further be used to calibrate and validate the computer-modeling efforts of the Chesapeake Bay Program.

The U.S. Geological Survey (USGS) began monitoring nutrients and suspended-solids in Virginia in 1984 in cooperation with the Virginia Department of Environmental Quality--Chesapeake Bay Office (VDEQ; at that time, the Virginia Water Control Board) to quantify loads entering Chesapeake Bay from its major tributaries in Virginia. The initial monitoring program consisted of collecting water-quality data on a twice-per-month scheduled basis at sites near the Fall Line on four tributaries to the Bay: the James, Rappahannock, Pamunkey, and Mattaponi Rivers. The Fall Line is geographically defined as the point where the Piedmont Physiographic Province meets the Coastal Plain, and in most instances this corresponds to the point farthest downstream that is unaffected by tides. Loads estimated for rivers at the Fall Line can therefore be used as single-point sources of loads to the Chesapeake Bay. The monitoring program was expanded over the years to include smaller basins that are tributary to the Potomac, Rappahannock, Pamunkey, and James Rivers.

Loads of nutrients and suspended solids are greatest during stormflow conditions because of higher discharge and often higher constituent concentrations. Therefore, the monitoring program was expanded in 1988 to include more frequent water-quality data collection during stormflow conditions at two major Virginia tributaries to the Chesapeake Bay, the James and Rappahannock Rivers. In July of 1989, the Pamunkey, Mattaponi and Appomattox Rivers were added to this storm-monitoring network. In July of 2004, the North and South Fork Shenandoah, Rapidan, and James (at Richmond at the Huguenot Bridge) Rivers were added to the storm-monitoring network. In 2005, the James River at the Blue Ridge Parkway was added to the storm-monitoring network (DEQ continues to collect the monthly scheduled sample at the Blue Ridge Parkway Site). Also in 2005, the USGS began monthly monitoring of water-quality conditions at the North and South Fork Shenandoah and Rapidan Rivers. In 2006, the James River (at Richmond) station was moved from the Huguenot Bridge to the Boulevard Bridge for safety reasons (note that the stream gage was left at the Huguenot Bridge site). In 2007, the USGS began monthly and storm monitoring at the North Anna and Chickahominy Rivers as well as monthly monitoring at the James (at Richmond at the Boulevard Bridge) River (this monthly monitoring was previously done by DEQ). In 2010, the USGS began monthly and storm monitoring at Smith Creek. In 2011 the Rivanna River was added to the storm-monitoring network (DEQ continues to collect the monthly scheduled sample at the Rivanna River site). A parallel program has been conducted on 4 tributaries in Maryland by the USGS in cooperation with the Maryland Department of the Environment since 1982.

A seven-parameter log-linear-regression model (Cohn, 1989), which includes variables for discharge, seasonality, and time is used to provide estimates of constituent concentration on days when no concentration data are available. The product of estimated concentrations and daily mean discharge provides daily load estimates, which are then summed to provide monthly and annual

loads of selected nutrients and suspended solids. To evaluate long-term change in the input of these constituents, flow-adjusted trends in concentration are computed from the regression model (Langland and Others, 1999).

B. Objectives and Scope

The Chesapeake Bay River Input Monitoring Program is being used to define the magnitude, timing, and possible sources of nutrient inputs to the Chesapeake Bay from the non-tidal areas of the larger tributaries in Virginia. This sampling program provides a data base of selected constituents (nutrients and suspended solids) for periods of varying flow and season, which are used to produce estimates of constituent loading to the Chesapeake Bay.
The specific objectives of this program are to:

(1) describe concentrations of selected nutrients and suspended solids in terms of flow and season,
(2) compute monthly and annual loads of nutrients and suspended solids,
(3) compare concentration data and load estimates between rivers,
(4) compute trends in nutrient and suspended solid loads over time,
(5) explain possible factors influencing concentration, loads, and trends of nutrients and suspended solids,
(6) provide data for calibration of the Chesapeake Bay Watershed model and nutrient and sediment loading inputs to the Chesapeake Bay Water-Quality model.
(7) assess quality-assurance results in order to describe the quality of the analyses provided by the participating laboratories, and
(8) provide information needed to refine the network design for future monitoring programs for the Chesapeake Bay.

The stations monitored and their station numbers include:

(1) the James River at Cartersville	USGS 02035000, VDEQ 2-JMS157.28 (Discontinued sampling by DEQ 3/2001)
(2) the Rappahannock River near Fredericksburg	USGS 01668000, VDEQ 3-RPP113.37 (Discontinued sampling by DEQ 3/2001)
(3) the Appomattox River at Matoaca	USGS 02041650, VDEQ 2-APP016.38 (Discontinued sampling by DEQ 6/1999)
(4) the Pamunkey River near Hanover	USGS 01673000, VDEQ 8-PMK082.34 (Discontinued sampling by DEQ 4/2003)
(5) the Mattaponi River near Beulahville	USGS 01674500, VDEQ 8-MPN054.17 (Discontinued sampling by DEQ 4/2003)
(6) the North Fork Shenandoah River near Strasburg	USGS 01634000, VDEQ 1BNFS010.34
(7) the South Fork Shenandoah River at Front Royal	USGS 01631000, VDEQ 1BSSF003.56
(8) the Rapidan River near Culpeper	USGS 01667500, VDEQ 3-RAP030.21
(9) the James River at Blue Ridge Parkway	USGS 02024752, VDEQ 2-JMS279.41
(10) the James River near Richmond	USGS 02037618, VDEQ 2-JMS113.20
(11) the North Anna River at Hart Corner near Doswell	USGS 01671020, VDEQ 8-NAR005.42
(12) the Chickahominy River near Providence Forge	USGS 02042500, VDEQ 2-CHK035.26
(13) Smith Creek near New Market	USGS 01632900, VADEQ 1BSMT004.60
(14) the Rivanna River at Palmyra	USGS 02034000, VADEQ 2-RVN015.97

Water-quality sample collection began July 1, 1988, for the James (Cartersville) and the Rappahannock Rivers, and July 1, 1989, for the Appomattox, Pamunkey, and Mattaponi Rivers. Samples are collected once-per-month on a scheduled basis, which most often occurs during baseflow conditions. Samples also are collected during stormflow conditions, in order to cover a range in flow conditions. Stormflow water-quality sample collection began July 1, 2004, for the North and South Fork Shenanadoah, Rapidan, and James (Richmond) Rivers. In 2005, the James River at the Blue Ridge Parkway was added to the storm-monitoring network. Also in 2005, the USGS began monthly monitoring of water-quality conditions at the North and South Fork Shenandoah and Rapidan Rivers. In 2007, the USGS began monthly monitoring at the North Anna, Chickahominy, and James (at Richmond) Rivers as well as storm monitoring at the North Anna and Chickahominy Rivers. In April 2010, the USGS began monthly and storm monitoring at Smith Creek. In January 2011, the Rivanna River was added to the storm-monitoring network. Monthly and annual loads (based on a water year, October - September) of selected constituents are estimated using a seven-parameter log-linear-regression model (Cohn, 1989).

C. Data Usage

The data collected for the Virginia River Input Monitoring Program are used to help define the magnitude, timing, and sources of nutrient inputs to the Chesapeake Bay from the non-tidal areas of the major tributaries in Virginia. Additionally, this information can help gauge the success of

management practices aimed at reducing these inputs. These data provide a data base of selected nutrients and suspended solids collected during periods of varying flow and season, which are being used to estimate loads to the Chesapeake Bay of the selected constituents.

Concentration data and statistics from the concentration data will be used to describe the water-quality characteristics of each river, including concentration ranges and medians; the relations between concentration and discharge; and concentration and seasonality at each river. The load estimates will be compared to the loads from other rivers in the Chesapeake Bay, in order to see the relative differences between the basins. Differences may be examined using land-use information, discharge records, and possibly point and nonpoint sources of constituents. Trend estimates will be used to determine the changes in constituent inputs over the period of study, and to assess the impact of management practices implemented during that time.

Historical data may be used as background information for comparison purposes. Quality assurance data are used on an ongoing basis to evaluate field and analytical methods for representativeness, variance, bias, and accuracy.

D. Study Design and Rationale

The contributing basins for this report together comprise about 22 percent of the total Chesapeake Bay drainage area. The James and Rappahannock River basins represent approximately 13 and 4 percent of the Chesapeake Bay drainage area; the Appomattox, part of the lower James River Basin, represents another 2.5 percent; and the Pamunkey and Mattaponi River basins represent about 2 and 1 percent of the total Chesapeake Bay drainage area. The remaining percentage of Virginia within the Chesapeake Bay watershed is comprised of the Potomac River basin and its tributaries including the Shenandoah River, which are monitored by the USGS Virginia and Maryland Water Science Centers.

Table 1 presents the basin size, the percent land use in the Chesapeake Bay watershed, the percent land use in Virginia and the percent land use within each of the basins monitored for this report. The locations of the river basins and the River Input monitoring stations are shown in Figure 1. A description of each river basin and each sampling station follows.

Table 1. Land use for the Chesapeake Bay, the Chesapeake Bay watershed in Virginia, and selected major river basins in Virginia

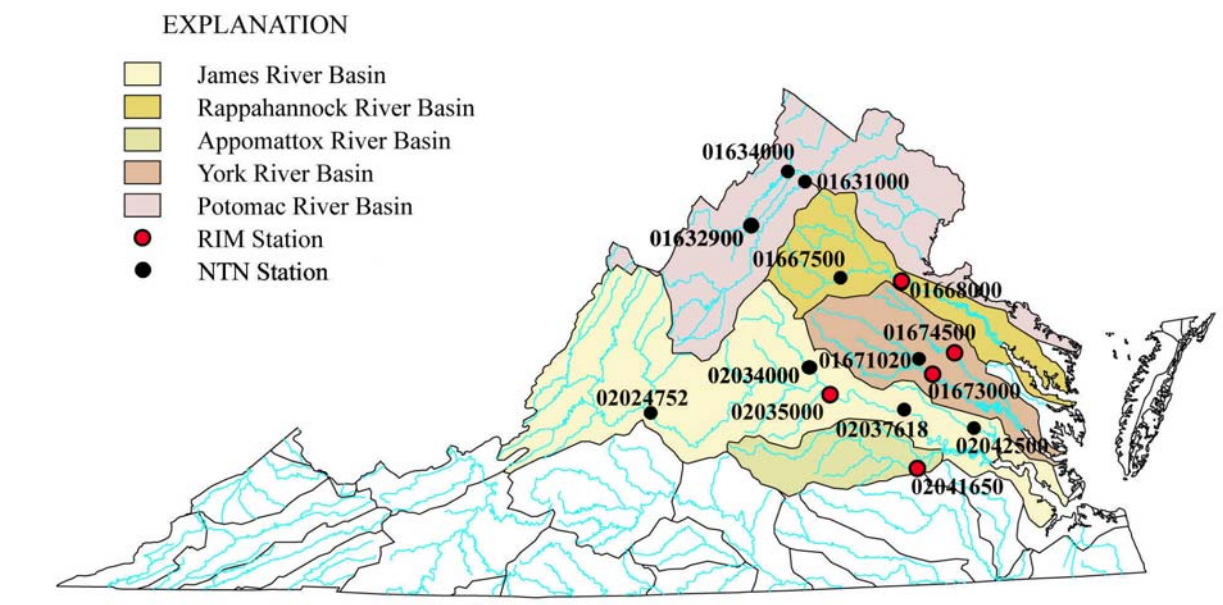
[mi^2, square miles;<, less than] (Neumiller and others, 1995; Chesapeake Bay Program, written commun.,1994)

Geographic area	Drainage Area (mi^2)	Urban (percent)	Agricultural (Herbaceous) (percent)	[a/] Forested (Woody) (percent)	Water (percent)	[b/]Total (percent)
Chesapeake Bay	64,000	8	33	58	1	100
Virginia	40,815	10	31	58	1	100
James River Basin	10,206	8	25	65	1	99
Rappahannock River Basin	2,848	6	40	54	<1	100
Appomattox River Basin	1,600	3	33	61	<1	98
Pamunkey River Basin	1,474	3	35	59	2	99
Mattaponi River Basin	911	2	27	69	<1	99

[a/] Includes wetlands.

[b/] Total percentage below 100 percent is possibly due to rounding and inaccuracies in area estimates.

Figure 1. Location of major river basins and the River Input Monitoring Stations.



The area of the James River Basin is approximately 10,206 mi^2, or about one-fourth of the area of Virginia, and is the third largest source of freshwater to the Chesapeake Bay, after the Susquehanna and Potomac Rivers. The James River Basin extends from the eastern part of West Virginia through four physiographic provinces (1) Valley and Ridge, (2) Blue Ridge, (3) Piedmont, and (4) Coastal Plain. The major cities in the James River Basin include Richmond, Lynchburg, Petersburg, Charlottesville, Williamsburg, Hopewell, and parts of Norfolk and Newport News.

The water-quality monitoring station at the James River near Cartersville, Va. (USGS station 02035000 and VDEQ station 2-JMS157.28 (Discontinued 3/2001)), represents the contributing area (6,257 mi^2) to the Chesapeake Bay from Virginia near the Fall Line, or about 60 percent of the James River Basin drainage area. This station is about 40 mi upstream of the Fall Line, but was selected because of the well-documented long-term flow record, and because there are no major streams contributing to the flow between this station and the Fall Line at Richmond. Because of the size of the basin upstream of the sampling station, streamflow varies widely, depending on precipitation patterns which may result in either very localized or widespread stormflow events. The average discharge at this site, computed during a period of 94 years, is 7,077 ft^3/s (Prugh and others, 1994). The location of this monitoring site is lat 37°40'16", long 78°05'09" (NAD83), which is at State Highway 45 at the Goochland/Cumberland County line, Va.

In 2004, one water-quality monitoring station was added in the James River Basin. This station is James River at Richmond (Huguenot Bridge, USGS station ID 02037500 and VDEQ 2-JMS117.35). In 2006, this station was moved downstream because of concerns over safety (note that the stream gage was left at the Huguenot Bridge site). This new station is James River at Boulevard Bridge at Richmond (USGS station 02037618 and VDEQ 2-JMS113.20). The drainage area for this watershed is 6,776 mi^2. The location of this monitoring site is lat 37°31'53", long 77°29'01" (NAD83) in Richmond, Va. In 2005, the water-quality monitoring station at the James River at the Blue Ridge Parkway, Va. (USGS station 02024752 and VDEQ station 2-JMS279.41) was added. The location of this monitoring site is lat 37°33'19", long 79°22'03" (NAD27) in Amherst County, Va. The drainage area associated with this station is 3,076 mi^2. In 2007, the water-quality monitoring station located at the Chickahominy River near Providence Forge (USGS station 02042500 and VDEQ 2-CHK035.26) was added. The drainage area for this watershed is 252 mi^2. The location of this monitoring site is lat 37°26'10", long 77°03'40" (NAD83) in New Kent County, Va. In 2011, the water-quality monitoring station at the Rivanna River at Palmyra (USGS station 02034000 and VDEQ 2-RVN015.97) was added. The drainage area for this watershed is 663 mi^2. The location of this monitoring site is lat 37°51'28", long 78°15'58" (NAD27), on State Route 15 in Fluvanna County.

The Rappahannock River Basin encompasses a land area of approximately 2,848 mi^2 which constitutes about 7 percent of the State of Virginia. The river flows from the eastern edge of the Blue Ridge physiographic province through the rolling hills of the Piedmont and Coastal Plain to the Chesapeake Bay, and is the second largest contributor of flow to the Chesapeake Bay from Virginia. The major cities or towns in the basin include Fredericksburg, Warrenton, Winchester, Culpeper, and Orange.

The Rappahannock River monitoring station (USGS station 01668000) is located upstream of Fredericksburg, Va. (This USGS station is at a cableway located 4.3 miles upstream of a VDEQ station (TF3.1 (Discontinued 3/2001)) at the Route-1 bridge; data from the VDEQ station is not used in this study). The area of the drainage basin upstream from the sampling station is approximately 1,596 mi^2, which is about 56 percent of the Rappahannock River basin. Upstream

from this station, most of the basin is in the uplands of the Piedmont Province, and because of the high relief, the river produces rapid or “flashy” streamflow peaks as a result of precipitation. The river therefore may carry large loads of suspended solids and other constituents relative to the size of the basin. The agricultural land use in the basin and expansion of the Washington, D.C., suburbs may increasingly affect the water quality of the river by causing elevated sediment concentrations in runoff, and an increase in concentrations of nutrients associated with the sediment, such as total phosphorus. The average discharge at this station is 1,660 ft^3/s, computed during a period of 86 years (Prugh and others, 1994). The location of the current sampling station and gage in Spotsylvania County, Va., is: lat 38°18'30", long 77°31'46" (NAD83).

In 2004, one additional water-quality monitoring station was added in the Rappahannock River basin. This new station is the Rapidan River near Culpeper, Va (USGS station 01667500 and VDEQ station 3-RAP030.21). The drainage area for this watershed is 472 mi^2. The location of this monitoring site is lat 38°21'01", long 77°58'30" (NAD83), which is at State Highway 522.

The Appomattox River Basin is within the James River basin, but because the Appomattox River enters the James River below the Fall Line, it is not included as a source to the James River monitoring station at Cartersville, and so is monitored separately. The basin area above the confluence with the James is 1,600 mi^2, approximately 16 percent of the James River basin and 4 percent of the area of Virginia. The Appomattox River basin begins in the Piedmont physiographic province, and flows through a small portion of the Coastal Plain before it flows into the James River near Hopewell. The Appomattox River basin is primarily rural, although the cities of Petersburg, Colonial Heights, and Hopewell are within the basin, downstream of the sampling station at Matoaca.

The drainage area of the Appomattox River basin above the sampling station at Matoaca (USGS station 02041650) is approximately 1,344 mi^2. The monitoring station is unique among the River Input Monitoring stations in that the flow is controlled by a dam at Lake Chesdin, 2.8 miles upstream of the sampling station. This tends to delay water-level rise from storms, so that the water level is very slow to rise and to fall in comparison to the other monitoring stations. Downstream of Lake Chesdin, the steep gradient due to the rapid elevation change, and a streambed of rocks and boulders result in expanses of rapids between the dam and the sampling station. The average discharge at this station is 1,384 ft^3/s, computed during a period of 23 years (Prugh and others, 1994). The location of the site in Chesterfield County is lat 37°13' 31", long 77°28' 31" (NAD83).

The total area of the York River Basin is approximately 2,650 mi^2, about 6.5 percent of Virginia’s total land area, consisting of the Pamunkey River, the Mattaponi River, and the coastal area below the sampling stations. Agriculture is an important component of the economy of the York River basin, and the area is primarily rural. Although the Pamunkey and Mattaponi Rivers are often collectively presented as the York and have many similarities, each river has unique basin, flow and water-quality characteristics. The Pamunkey and Mattaponi River basins are monitored above their confluence to form the York, and are reported separately for this study.

The total area of the Pamunkey River Basin is 1,474 mi^2, or about 4 percent of Virginia. The Pamunkey River basin begins in the lower part of the Piedmont Province where the relief is relatively low and extends into the Coastal Plain. The basin contains expanses of forested wetlands and marshes that are significant sources of wildlife productivity (Virginia Water Control Board, 1988). Ashland and Mechanicsville are the two major towns in the basin.

The Pamunkey River basin monitoring station (USGS station 01673000 and VDEQ station TF4.1 (VDEQ, Discontinued 3/2001)) is located near Hanover, Va. The area of the drainage basin above the sampling station is approximately 1,081 mi^2, which is about 40 percent of the York River basin. The low relief and relatively wide basin tend to produce stormflow peaks that are slow to peak and to recede. There is some regulation of the Pamunkey River from the dam at Lake Anna, approximately 100 mi upstream of the monitoring station, on the North Anna River. The average discharge at this station is 1,110 ft^3/s, computed during a period of 21 years (Prugh and others, 1994). The location of the site in Hanover County, Va., is lat 37°46' 04", long 77°19' 56" (NAD83).

In 2007, one additional water-quality monitoring station was added in the Pamunkey River basin. This new station is the North Anna River at Hart Corner near Doswell, Va (USGS station 01671020 and VDEQ station 8-NAR005.42). The drainage area of this watershed is 462 mi^2. The location of this monitoring site is lat 37°51'00", long 77°25'41" (NAD83) in Hanover County, VA.

The Mattaponi River basin is 911 mi^2, or two percent of the area of Virginia, and also is located within both the Piedmont and Coastal Plain physiographic provinces. Like the Pamunkey River, it tends to have expanses of wetland areas (VWCB, 1991). The wetland areas tend to slow flow velocities, and the hydrographs during storms are slower to peak and recede than at the Pamunkey River.

The Mattaponi River monitoring station (USGS station 01674500 and VDEQ station TF4.3 (VDEQ, Discontinued 3/2001)) is located near Beulahville, Va. The area of the drainage basin above the sampling station is approximately 601 mi^2, which is about 23 percent of the entire York River basin, and two percent of the area of Virginia. Like the Pamunkey, the Mattaponi River basin has expanses of freshwater wetlands (VWCB, 1991). The average discharge at this station is 583 ft^3/s, computed during a period of 50 years (Prugh and others, 1994). The location of the site in King and Queen County is lat 37°53' 16", long 77°09' 47" (NAD83).

In 2004, two additional water-quality monitoring stations were added in the Shenandoah River Basin. The first station is the North Fork Shenandoah River near Strasburg, Va. (USGS station 01634000 and VDEQ station 1BNFS010.34). The drainage area for this watershed is 768 mi^2. The location of this monitoring site is lat 38°58'36", long 78°20'10" (NAD83), which is at state Highway 55 in Warren County, Va. The second station is the South Fork Shenandoah River at Front Royal, Va. (USGS station 01631000 and VDEQ 1BSSF003.56). The drainage area for this basin is 1,642 mi^2. The location of this monitoring site is lat 38°54'50", long 78°12'39" (NAD83), which is at State Highway 619 in Warren County, Va. In 2010, a monitoring station was added at Smith Creek near New Market (USGS station 01632900 and VDEQ 1BSMT004.60). The drainage area of the watershed is 93.6 mi^2. The location of this monitoring site is lat 38°41'36", long 78°38'35" (NAD27), on State Route 620 in Shenandoah County.

E. Description of Streamflow

Constituent concentrations within a river change as a function of streamflow, and streamflow data are necessary to compute constituent loads. A streamgage is currently operated at each of the network monitoring stations; these streamgages are operated as a joint network by USGS and VDEQ, following USGS protocols. Realtime streamflow data are available online at: http://waterdata.usgs.gov/va/nwis/rt/.

F. Monitoring Parameters and Frequency of Collection

Table 2 shows the constituents monitored for this study, the detection limits at each laboratory, and the reference to the method used.

RIM Samples are analyzed for the following constituents:

Nitrogen species --particulate nitrogen, total dissolved nitrogen, dissolved ammonia nitrogen, dissolved nitrite plus nitrate, dissolved nitrate, total nitrogen. (Prior to February 1996, total Kjeldahl nitrogen - ammonia plus organic species - was also determined). The concentration of dissolved nitrite is the difference of dissolved nitrite plus nitrate concentration and dissolved nitrate concentration.

Phosphorus species --particulate phosphorous, total dissolved phosphorous, dissolved orthophosphorus, particulate inorganic phosphorus, total phosphorus.

Other species -- dissolved silica, particulate carbon, particulate inorganic carbon, dissolved organic carbon, chlorophyll a, total suspended solids, fixed suspended solids, suspended sediment and percent fines (RIM sites - Processed by the USGS sediment lab in Louisville, Kentucky. Add-on sites - processed by the Virginia Consolidated Laboratories).

RIM Add-On Samples are analyzed for the following constituents:

Nitrogen species --total nitrogen, total ammonia, and total nitrate and nitrite.

Phosphorus species --dissolved orthophosphorus and total phosphorus.

Other species -- Suspended sediment - processed by the Virginia Consolidated Laboratories for total suspended solids, fixed suspended solids, suspended sediment and percent fines.

Approximately 40 samples per year were initially needed to accurately estimate loads using the log-linear regression model selected for this study. Emphasis was placed on sampling throughout the range in storm conditions that existed throughout the sampling period. Currently 20 samples per year are needed to accurately estimate loads using the log-linear regression model selected for this study and utilizing the data previously collected for this project. All stations will have 20 water-quality samples collected each year. These 20 samples will be comprised of 12 routine samples and 8 stormflow samples. In addition to the once-per-month routine samples, up to 2 storm samples may be collected on either the rise, peak, or fall of a given storm hydrograph. This allows for the identification of the variability associated with each water-quality constituent over a wide range of stormflow events.

Appendix 1 shows an example of the record of field data planned, including quality assurance data. This form is also used by field personnel to document that the sample was collected. This record is kept for each of the stations.

G. Continuous Water-Quality Monitoring

In 2007, continuous water-quality monitors were added to the existing RIM project at the James River at Cartersville, Rappahannock River at Fredericksburg, and Pamunkey River near Hanover RIM stations. The Rappahannock River monitor was discontinued in 2009. In April 2010, a continuous water-quality monitor was deployed on Smith Creek. These YSI-6920 monitors are depolyed in situ and collect values every 15 minutes for pH, specific conductance, turbidity, and water temperature. These water-quality data are stored in the USGS NWIS database and also are available at http://nwis.waterdata.usgs.gov/va/nwis/rt. An USEPA Chesapeake Bay program approved Quality Assurance Project Plan is already in place for continuous water-quality monitoring ("Enhanced sediment collection for improving continuous sediment simulations - Quality Assurance/Quality Control Project Plan, December 2005"). A copy of the quality assurance/quality control plan is provided in Appendix 5.

Table 2. Virginia River Input Monitoring Program Detection Limits

Analyte	NWIS Code (storet code)/ CEDS Code	VDCLS Analytical Method	Detection Limit[1/]	VDCLS Parameter Group[6]	Container
Dissolved Ammonia Nitrogen	00608/ 00608[5]	EPA 350.1	.006 ppm	CNTF2	250 mL plastic bottle (HDPE) Filter Immediatley and Preserve at 4°C
Dissolved Nitrate+Nitrate	00631/ 631[5]	EPA 353.2	.004 ppm		
Dissolved Nitrite	00613/ 00613	EPA 353.2	.002 ppm		
Dissolved Orthophosphorus	00671/ 00671	EPA 365.1	.002 ppm		
Dissolved Silica	00955/ 00955	Standard Methods 4500-Si F (17th Ed.)	.1 ppm		
Particulate Nitrogen	00601/ PNWLF	EPA 440.0	0.03 ppm	BAYR2	1 gallon Cubitainer Preserve at 4°C
Total Dissolved Nitrogen	00602/ TDNLF	Colorimetric, Chesapeake Bay (D'Elia[2/])	.011 ppm		
Particulate Phosphorus	00667/ PPWLF	Colorimetric, Chesapeake Bay (Aspila[3/])	.0013 ppm		
Particulate Inorganic Phosphorus	/ PIPLF	Colorimetric, Chesapeake Bay (Aspila[3/])	.0008 ppm		
Total Dissolved Phosphorus	00666/ TDPLF	Colorimetric, Chesapeake Bay (Valderrma[2/])	.003 ppm		
Particulate Carbon	00694/ PCWLF	EPA 440.0	0.05 ppm		
Particulate Inorganic Carbon	00688/ 00688	EPA 440.0	0.02		
Total Suspended Solids	00530/ 00530	Standard Methods 2540 D (17th Ed.)	3 mg/L		
Volatile Suspended Solids	00535/ 00535	Standard Methods 2540 D (17th Ed.)	3 mg/L		
Fixed Suspended Solids	00540/ 00540	Standard Methods 2540 D (17th Ed.)	3 mg/L		
Turbidity	00076/ 82079	EPA 180.1	0.01 NTU		

Analyte	NWIS Code (storet code)/ CEDS Code	VDCLS Analytical Method	Detection Limit[1/]	VDCLS Parameter Group[6]	Container
Dissolved Organic Carbon	40573/ 00681	Standard Methods 5310 B (18th Ed.)	.36 ppm	DOCFF	4 oz. amber glass bottle (baked) Acid preservation (HCl)
Chlorophyll A	70957/ 32211	EPA 1002-G	.4 ppm	FCHLR	1 - 3 0.7um GF/F glass fiber filter (total vloume filtered = 300 mL)
Total Nitrogen	000600/ 000600	EPA Standard Method 4500-N Part C (20th ed)		BAYR2	See Above
Total Phosphorus	00665/ 00665	EPA 365.4	0.01 ppm	TPLL	125 mL plastic bottle (HDPE) Preserve with H_2SO_4 and store at 4^oC
Suspended Sediment	80154/ SSC-Total	ASTM 3977-97 Method B		SSC	1 pint wide mouth glass bottle (USGS), or 500 mL clear plastic bottle (DCLS)
Suspended Sediment - Coarse > 62um	/ SSC-Coarse	ASTM 3977-97 Method C		SSC	From Suspended Sediment bottle
Suspended Sediment - Fine < 62um	70331/ SSC-Fine	ASTM 3977-97 Method C		SSC	From Suspended Sediment bottle

[1/] Detection limits are determined on a yearly basis by VDCLS, using the procedure found in Appendix B of EPA CFR Part 136

[2/] D'Elia, C.F., P.A. Steudler and N. Corwin. 1977. Determination of Total Nitrogen in Aqueous Samples Using Persulfate Digestion. Limnol. Oceanogr. 22:760-764.

[3/] Aspila, Agemian and Chau, 1976. A semi-automated method for the determination of inorganic, organic, and total phosphate in sediments. Analyst 101:187-197.

[4/] Valderrama, J.C. 1981. The simulataneous analysis of total nitrogen and total phophorus in natural waters. Mar. Chem. 10:109-122.

[5/] The Add-on samples are whole water samples and the results are stored as total concentrations, rather than dissolved concentrations.

[6/] A BAYT3 container (Add-on samples) is analyzed for 00530, 00540, 00631, 00608, 00600, 00671.

II. PROJECT ORGANIZATION AND RESPONSIBILITY

The organization of the project for the Virginia River Input Monitoring Program is outlined in the diagram below. The duties of the individuals are also described below.

Project Officer
Frederick Hoffman
Chesapeake Bay Office/ VDEQ
804-698-4334
Fax 804-698-4032

Principal Investigators
Kenneth E. Hyer and Douglas L. Moyer
U.S. Geological Survey, WRD
*804-261-2636 or 804-261-2634
*Fax 804-261-2657

Field Sampling	Laboratory Analysis	Data Management	Data Analysis
USGS *Hydrologic Technicians and Hydrologists as needed	VDCLS Jay Armstrong 804-648-4480 (Nutrients) Chris Morton 804-648-4480 (Solids) Bailey Davis - Carbon and Chlorophyll A 804-648-4480	USGS *Hydrologist (2) Hydrologic Technician	USGS *Hydrologist (3)
	USGS KY Sediment Lab 502-493-1944	VDEQ Cindy Johnson 804-698-4385	USGS, Baltimore, MD Hydrologist 443-498-5560

*same phone and fax numbers as above

VDEQ, Virginia Department of Environmental Quality, Richmond, VA;
USGS, U.S. Geological Survey;
VDCLS, Virginia Division of Consolidated Laboratory Services, Richmond, VA;

PROJECT OFFICER

Frederick Hoffman
Virginia Department of Environmental Quality
Box 1105
Richmond, VA 23218

804-698-4334
Fax 804-698-4032

Responsible for overseeing the administrative aspects of the program including fiscal management, coordination among other administrators, and coordination with cooperating agencies and institutions. Approves technical design, conduct, and data analysis of the program.

PRINCIPAL INVESTIGATORS

Kenneth E. Hyer - 804-261-2636
Douglas L. Moyer - 804-261-2634
U.S. Geological Survey, WRD
1730 East Parham Road
Richmond, VA 23228
Fax 804-261-2657

Responsible for the technical design, conduct, and data analysis of the program. Provides guidance to other key personnel and directs the efforts to organize, describe, and interpret the results of the monitoring. Has ultimate responsibility for quality assurance.

FIELD SAMPLING

Hydrologic Technician(s), U.S. Geological Survey, Richmond, VA
Other Hydrologists and Hydrologic Technicians as needed

Coordinate all field activities of the program, including procuring all necessary equipment, collecting water samples according to the USGS sampling protocol, measuring field parameters, and coordinating all field quality assurance data collection.

LABORATORY ANALYSIS
Virginia Division of Consolidated Laboratories (VDCLS), Richmond, VA

Jay Armstrong - Nutrients
Chris Morton - Solids
Bailey Davis - Carbon and Chlorophyll A

Complete laboratory analyses on a timely basis and return analytical results to VDEQ-CBO. Provide assistance with information concerning analytical techniques for constituents.

USGS National Water Quality Laboratory (NWQL), Denver, CO

John Vasquez, Supervisory Chemist - Nutrients
Harold Ardourel, Supervisory Chemist - Solids

Provides standard-reference samples to VDCLS.

USGS Kentucky Sediment Laboratory

Aimee Downs, Geographer

Provides suspended sediment data for the primary RIM stations.

DATA MANAGEMENT
Hydrologist(s), U.S. Geological Survey, Richmond, VA
Hydrologic Technician, U.S. Geological Survey, Richmond, VA

Cindy Johnson, Virginia Department of Environmental Quality, Richmond, VA

Responsible for maintaining the Virginia data base and transferring and checking all data from VDCLS to the USGS. Responsible for facilitating the transfer, collation, and retrieval of the data. Responsible for quarterly progress reports to VDEQ.

DATA INTERPRETATION
Hydrologist(s), U.S. Geological Survey, Richmond, VA
Hydrologist, U.S. Geological Survey, Baltimore, MD

Responsible for graphing, presentation and interpretation of the data; application of quality assurance data; and all formal report requirements for the program.

III. QA OBJECTIVES AND CRITERIA

Because data collected for the Virginia River Input Monitoring Program are used to (1) help define the magnitude and timing of nutrient inputs to the Chesapeake Bay at the Fall Line and (2) to provide a data base of selected constituents collected during periods of varying flow and season, several general quality assurance objectives are necessary in order for the program to be successful.

For Laboratory precision and accuracy, the Virginia Division of Consolidated Laboratories (DCLS) replicated approximately 10% of the samples and 5% of the samples analyzed are spiked samples. Detailed descriptions of the quality assurance practices for each of the analytical procedures conducted by DCLS, can be found in the following SOPs:

Method 2506 Determination of Carbon and Nitrogen in Particulates of Estuarine/ Coastal Water Using Elemental Analysis. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2-510 The Determination of Chlorophylls A, B, & C in Marine and Freshwater Algae by Visible Spectrophotometry.Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2523 Determination of Ammonia Nitrogen by Automated Colorimetry. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2525 Total Dissolved Nitrogen and Method 2540 Total Dissolved Phosphorus Automated Colorimetric. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2526 Nitrate Plus Nitrite Nitrogen in Estuarine and Coastal Waters Low level, Automated. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2532 Carbon – Total Organic and Dissolved Organic Carbon. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2538 Phosphorus - Orthophosphate Low Level, Automated. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2539 Determination of Phosphorus in Sediments and Particulates of Estuarine/Coastal Waters. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2543 Molybdate Reactive Silica in Water and Wastewater. Commonwealth

of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

DCLS 2544 Total Suspended Solids. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2590 Determination of Inorganic Carbon in Particulates of Estuarine/ Coastal Waters Using Elemental Analysis. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

Method 2591 Determination of Inorganic Phosphorus in Sediments and Particulates of Estuarine/Coastal Waters. Commonwealth of Virginia. Department of General Services. Division of Consolidated Laboratory Services.

A. Comparability of Results

The data collected for this program must be comparable and reproducible. Therefore, sampling methods and sample analyses must be uniform and consistent among the agencies collecting and analyzing the data. This plan includes (1) a field component to assure that water quality samples are representative of river conditions and (2) a laboratory component to assess the variance, accuracy, and bias of analytical results.

The field component consists of documentation of field conditions, collection procedures, and equipment as follows:

(1) Water quality samples are collected using approved USGS guidelines to ensure the collection of samples that are representative of the river cross-section. These guidelines assure the collection of a representative, composite sample from the horizontal and vertical cross section of the river.

(2) Sampling criteria based on flow characteristics are documented for field personnel to ensure that water-quality samples are collected over a range in flow conditions. In addition, detailed recording of field procedures ensures consistency of procedures between field personnel.

(3) Proper use of sampling and monitoring equipment and sample collection techniques by field personnel is verified with in-house testing (field audits) of field procedures.

(4) Proper cleaning procedures of sampling equipment is documented through ongoing comparisons of field and equipment blanks, scheduled as in Appendix 1.

The laboratory component of this plan consists of the collection and analysis of duplicate and standard-reference samples as follows, and as scheduled in Appendix 1:

(1) Concurrent Replicate samples are used to document the variance of the analytical results. Replicate samples are prepared by collecting to concurrent samples. Both samples are then analyzed by VDCLS. The second subsample is disguised as an environmental sample by labeling it with a different time from the first subsample.

(2) Standard-reference samples document the ability of a laboratory to accurately analyze samples of known concentrations and to check for bias in analytical results. Standard-reference samples are prepared in the USGS laboratory and submitted to VDCLS and NWQL for analysis.

In addition to the field and laboratory components of the quality assurance plan, there is also in-house checking of data that are received from the laboratory. All data are logged in as they arrive from VDCLS, then later are reviewed for transcription errors and corrected.

Concentrations below the minimum reporting limit ("censored" data) are considered in the regression model to be equal to the minimum reporting limit as long as fewer than 25 percent of the data are censored. The adjusted maximum likelihood estimator (AMLE) is used in the few cases where censoring is greater than 25 percent (Helsel and Cohn, 1988). In summations of total nitrogen and total phosphorus from their respective dissolved and particulate constituents, the sum is taken to be a value less than the combined minimum reporting limits if both the particulate and dissolved values are censored ($<V_1 + <V_2 = <(V_1+V_2)$). If just one value is censored, the sum is considered to be the uncensored value plus half the minimum reporting limit for the censored value ($<V_1 + V_2 = <(V_1 + V_2)$). However, total nitrogen for the time period 1985 - 1996 is determined as the sum of total kjeldahl nitrogen (TKN) and nitrate plus nitrite (DNOx). Censored data handled as follows: if DNOx is < 0.041 mg/L then TN = TKN else TN = <(TKN + DNOx).

Calculations for all replicate data are also performed with the censored data equal to zero in order to define the range of variance for each constituent. Concentrations that appear to be outliers are reexamined, using the field notes to determine the presence of any unusual circumstances or hydrologic conditions. If there is no indication of anything out-of-the-ordinary, the laboratory is asked to review their records for accuracy. If necessary, data are corrected and changes are documented with the rationale and source of changes made.

B. Completeness of Sampling

A complete data set is needed to meet the objectives of the project. In particular, the suites of analyses must be comprehensive, and the sampling coverage must capture the variability of both base-flow and high-flow instantaneous loadings of the constituents. Completeness is documented by:

1. Periodic checks by the project water-quality data base manager which assess the completeness and accuracy of calculations for the analyses.
2. Assessment of the number of samples collected versus the number of samples received. An ongoing list is kept to make sure that all analyses are received from VDCLS. Periodically, this list is sent to VDCLS and VDEQ, for their information and use.
3. Development of as complete and representative a data set as possible, covering all streamflow conditions.
4. Collection of field and quality-assurance data on a scheduled basis, with documentation of each sample as shown in Appendix 1.

C. Representativeness

The collection of water-quality samples representative of river conditions is essential. Samples therefore are collected using approved USGS protocols for water-quality sampling, ensuring that water-quality conditions are represented as closely as possible.

Water-quality samples are collected during baseflow by the VDEQ at the James River at Blue Ridge Parkway and Rivanna River stations, and by USGS (all other sites) during baseflow and stormflow conditions. The USGS collects all water-quality samples using an equal-width increment (EWI) method, so that a sample representative of stream conditions is obtained. The EWI method, in which samples are collected at centroids of equal-width increments of the stream, is used most often in shallow or sandbed streams where the distribution of water discharge in the cross-section is not stable, or in streams where the distribution of discharge in the cross-section is unknown. Samples are collected using a USGS-designed depth-integrating sampler (designation DH-95 or D-96) when average streamflow velocities exceed 1.5 ft/s, or a weighted sample bottle (WBH-96) at lower velocities when depth-integrating samplers are not effective. A depth-integrating sampler is designed to sample the vertical water column of the river proportionally to the velocity at each depth. These methods are documented by Edwards and Glysson (1988) and Ward and Harr (1990).

The VDEQ collects all water-quality samples using a single depth integrated or depth and width integrated techniques. For further details on the VDEQ sampling protocol please refer to the "Virginia CBP Non-Tidal Network Quality Assurance/Quality Control Project Plan for the Time Period of July 01, 2010 - June 30, 2011".

IV. SAMPLING PROCEDURES

Water-quality samples are collected according to established U.S. Geological Survey sampling protocol for nutrients and suspended solids. These methods are documented in the publications *Field methods for measurement of fluvial sediment*, by T.K. Edwards and D.G. Glysson, 1988; U.S. Geological Survey Open-File Report 86-531, in *Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses*, by J.R. Ward and Albert Harr, 1990, U.S. Geological Survey Open-File Report 90-140; and in *U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water*, by A.J. Horowitz and others, 1994, U.S. Geological Survey Open-File Report 94-539. More recently, all USGS field protocols have been summarized in a National Field Manual that is available online at: http://water.usgs.gov/owq/FieldManual/index.html.

Samples are collected in a manner ensuring that they are representative of river conditions, which involves collecting horizontally and vertically integrated samples. Sampling equipment is made from non-contaminating materials, which includes epoxy-coated depth integrated samplers for collection of the nutrients and suspended solids samples. Nutrients samples are filtered in the field using an in-line, 0.45 um Gelman capsule filter. All samples are preserved on ice and taken to VDCLS on the same day if possible, or as soon as feasible. (NOTE: Samples prior to January 15, 1994, were filtered in the VDCLS laboratory. After that date, field filtering using the Gelman filter was instituted as part of the procedure.)

Because of variations in flow conditions, width of each streambed, and differences in cross-sectional morphology, sampling procedures between all rivers differ. Protocols were developed for each site, outlining where samples are to be taken in the cross section, what type and size of sampler to use, how samples are to be labeled, and the number of samples to collect, in order to ensure that all personnel responsible for sampling use the correct procedures.

Field parameters (pH, specific conductance, dissolved oxygen, turbidity, and water temperature) are collected at alternating stations along the stream channel cross section. These parameters are collected using a YSI multi-parameter field meter and following standard U.S. Geological Survey protocols (Appendix 4).

V. SAMPLE CUSTODY

Samples are collected in plastic “cubitainers”, labeled using a VADEQ tag, immediately put on ice and transported to the VDCLS laboratory. Hydrochloric acid and sulfuric acid are used to preserve the dissolved organic carbon and total phosphorus samples, respectively. At those times when it is impossible to take samples to the laboratory, samples are refrigerated at 4° C and taken to the laboratory as soon as possible. A Virginia Water Science Center field form is completed and kept on file in the Virginia Water Science Center as a record of the samples collected, to check for final completeness of the analyses, and to record field measurements, date and time of collection, and any unusual conditions. Associated field data are entered into and sample analyses are scheduled using the VADEQ Comprehensive Environmental Data System (CEDS). Suspended-sediment samples for RIM stations are collected in a 1-pint glass bottle, labled and sent to the USGS sediment laboratory in Louisville, Kentucky. No preservation is necessary for suspended-sediment samples.

VI. CALIBRATION PROCEDURES AND FREQUENCY

Field parameters (pH, Specific Conductance, Water Temperature, Turbidity, and Dissolved Oxygen) are calibrated in the field using a YSI 6920 multiparameter instrument before field data are collected. An equipment calibration log is kept with each multiparameter instrument. This log records the date, results of the calibration, identification of standards, initials of field person, and any corrective actions taken. Both pH and specific conductance standards are supplied by the USGS NWQL in Denver, CO; each standard has expiration dates posted on its container.

Calibration of laboratory equipment at VDCLS is documented in the publications entitled *Quality Assurance Plan for the Virginia Division of Consolidated Laboratory Services*, 1982, and *Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments*, by F.C. Friedman and D.E. Erdmann, Washington, U.S. Govt. Print. Off., 1982.

Calibration of the laboratory equipment at the USGS sediment lab in Louisville, KY is documented in the publication entitled *Quality-Assurance Plan for the Analysis of Fluvial Sediment by the Northeastern Region, Kentucky District Sediment Laboratory*, C.J. Sholar and E.A. Shreve: Open-file report 98-384, Louisville, Kentucky 1998.

Calibration of laboratory equipment at NWQL is documented in the publications entitled *Quality Assurance Practices for the Chemical and Biological Analyses of Water and Fluvial Sediments*, by F.C. Friedman and D.E. Erdmann, Washington, U.S. Govt. Print. Off., 1982; and in *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*, M.J. Fishman and L.C. Friedman: Open-file report 85-495, Denver, 1985.

VII. ANALYTICAL PROCEDURES

The majority of samples collected are analyzed by VDCLS. Samples collected prior to January 15, 1994 were filtered and analyzed by VDCLS under criteria established by Clesceri, Greenberg, and Trussell (1989) and the USEPA Environmental Monitoring and Support Laboratory (1983). Beginning January 15, 1994, samples have been filtered in the field using procedures established by Horowitz and others (1994) before being delivered to the laboratory for analysis.

Requirements set by the USEPA for regulatory laboratories state that nutrient samples be filtered within 24 hours and suspended-solids determinations be performed within 7 days. Samples collected on weekends are chilled to 4°C and held until they can be accepted by VDCLS the following week.

In some instances, the analytical method for certain constituents differs for the total constituent and the dissolved constituent. For each analytical method there is a range within which the actual concentration is expected, so that it is possible for the analytical result of the total concentration of a particular constituent to be less than that of the dissolved concentration for that constituent. Minimum reported concentrations may differ according to the detection limit, depending on the specific technique done by the laboratory. VDCLS has Standard Operating Procedures (SOP) for each laboratory analyte. The reference for each laboratory analyte SOP can be found in Section III (QA Objectives and Criteria).

The concentration of total nitrogen for this project is computed as the sum of particulate nitrogen and dissolved nitrogen for VDCLS samples and as the sum of dissolved nitrite-plus-nitrate nitrogen concentration and total ammonia-plus-organic (Kjeldahl) nitrogen concentration for NWQL samples. Prior to February 1996, total nitrogen was computed as the sum of dissolved nitrite-plus-nitrate nitrogen concentration and total Kjeldahl nitrogen concentration for VDCLS samples. Total phosphorous is computed as the sum of particulate phosphorous and dissolved phosphorous.

VIII. DATA REDUCTION, VALIDATION, AND REPORTING

Samples are collected, preserved and transported according to accepted SOP methods to DCLS Central Receiving by the USGS. Central Receiving (DCLS) personnel log in samples and distribute them to the appropriate laboratory for analysis. After analysis, the data results are transformed into the correct concentration units, keyed into the LIMS system (Laboratory Information Management System) by the chemist completing the analysis and reviewed by the appropriate laboratory personnel. Upon approval the results are shipped back to VADEQ via FDT transfer and entered into the CEDS2000 database. In the event data sheets are utilized to submit the samples to DCLS (e.g. due to a CEDS/WQM system failure) the results are printed out onto laboratory sheets and given to the VADEQ Laboratory Liaison. Results returned on paper are keyed into the CEDS2000 system by personnel in the Water Division and forwarded to the appropriate region or the Central office project manager.

Data go through a series of screens and reviews to identify invalid, qualified or QA supported data by both DEQ and USGS personnel. The qualified and QA supported data are then entered into the QWDATA water-quality data base.

The USGS Virginia Water Science Center field sheet that details field conditions and field parameter values is completed for each sampling trip and kept in the USGS Office along with a copy of the analytical services request forms. The field parameter values are entered into the Virginia Water Science Center QWDATA water-quality data base at the office.

Water-quality analyses performed are stored on the USGS Virginia Water Science Center QWDATA water-quality data base. Raw data are published in the USGS Annual Report for Virginia. The appropriate data originator is notified of errors so that the source data bases can be corrected and thus remain consistent with all others.

IX. INTERNAL QC CHECKS

A. Field

The quality assurance practices of field procedures include documentation of cross-section, depth-integrated variability; quality assurance of field personnel; documentation of field sampling status; and collection of field, equipment, and laboratory blanks. These practices are described in greater detail in Section III.

B. Laboratory

VDCLS--The quality assurance practices of VDCLS including quality control, quality assurance of analytical results, quality assurance of all materials used in the preservation and containment of water-quality samples, and the blind- reference sample quality assurance program, are documented in *Quality Assurance Plan for the Virginia Division of Consolidated Laboratory Services.* In each laboratory analyte SOP (see section III QA Objectives and Criteria), there is a quality control section that addresses a) assessing laboratory performance, and b) assessing analyte recovery and data quality. Most analytical procedures used are referenced in *Chemical Analysis for Water and Wastes*: USEPA-600/4-79-020, Environmental Protection Agency, 1979, and *Standard Methods for the Examination of Water and Wastewater* (17th ed) edited by Clesceri et al., 1989.

USGS Sediment Laboratory in Kentucky -- The quality assurance practices of the USGS sediment lab are documented in the Open-File report entitled *Quality-Assurance Plan for the Analysis of Fluvial Sediment by the Northeastern Region, Kentucky District Sediment Laboratory,* OFR 98-384, by C.J. Sholar and E.A. Shreve, 1998. Included in this publication are: analytical methods development procedures; standard quantitative analysis techniques; instrumental techniques; laboratory quality control; quality assurance monitoring; documentation, summary, and evaluation of data; and material evaluation.

Quality assurance of analytical results received from the participating laboratories incorporate both quality control and quality assurance monitoring. Quality-control monitoring is accomplished through the use of a personal and a computerized data review. Several computer checks are made which “flag” a possible error in analysis. These flags are documented on the analytical report specific to each sample. The completed analytical report is then reviewed by NWQL quality-assurance personnel prior to its release from the laboratory. The reviewers judge whether there is a reason for the data to have “failed” a check. If analytical error is suspected, a re-run of the sample is requested. Quality-assurance monitoring is also performed by the requestor of the analysis, whose familiarity with the site may allow them to identify an error that was not apparent to the laboratory personnel. If an error is found with the analysis, a re-run is requested.

Quality assurance of all materials used in the preservation and containment of water samples is performed by the USGS laboratory. Preservation materials, such as sulfuric acid, and sample bottles are randomly sampled by lot or batch number for any elevated trace metals and major cations and anions that may be present. If elevated levels are indeed found in either of these, the laboratory conducts additional sampling of the preservation materials and bottles, and if necessary, recalls them.

VDCLS participates in a nation-wide Standard-Reference Sample (SRS) quality-assurance program. This program was designed to evaluate the performance of each participating laboratory

as well as monitor long-term trends in the bias and accuracy of analytical methodologies. Samples are prepared at the NWQL, Denver, CO. Samples are prepared by the USGS Branch of Quality Assurance from which they are subsequently distributed to laboratories across the country. Results are published twice yearly and distributed to each participating laboratory and USGS Offices in each state.

X. PERFORMANCE AND SYSTEM AUDITS

Project reviews are conducted quarterly by USGS staff, and periodically by the USGS Area Water-Quality Specialist. USGS technical reviews are conducted periodically at the request of the principal investigator.

A Water Science Center Water-Quality Review is held every three years by the USGS Regional Water-Quality Specialist and Regional Staff. Field methods are observed for consistency with national USGS procedures, and the Center water-quality data base is examined for agreement between laboratory and field data.

The project officer and other staff from VDEQ are kept informed of the status of the project on a quarterly basis by the development of a quarterly report detailing the number of samples collected per site and any problems associated with sampling or analysis.

VDCLS and the USGS Kentucky Sediment Laboratory participate in the Standard-Reference Sample quality-assurance program that analyzes the laboratory's performance as described previously.

XI. PREVENTIVE MAINTENANCE

Preventive maintenance of field instruments is done on a routine basis to ensure that the instruments remain in good working order. All potentially fragile electrodes and cells are stored in such a manner as to prevent breakage. Additionally, they are kept clean and free from any build-up that may affect their performance; rejuvenation of electrodes is performed periodically. All field meters and calibration standards are removed from vehicles and brought indoors after use to avoid mechanical or electronic problems caused by extremes in temperature. Batteries are changed and/or units recharged regularly.

All field instruments are calibrated prior to use, as described in Section VI, Calibration Procedures and Frequency. If an instrument is not in good working order, spare instruments are readily available so that there is no interference with field operations. Instruments in need of repair are repaired in a timely manner.

XII. ASSESSMENT OF DATA VARIABILITY, BIAS, ACCURACY, REPRESENTATIVENESS, AND COMPLETENESS

Assessment of data variability and bias for the Virginia River Input Monitoring Program consists of collecting and analyzing duplicate and blank samples. The purpose of these quality assurance practices is to quantify the variability of results from VDCLS, the major laboratory that provides analyses for this study, and to check for bias at VDCLS.

Between 5 and 10 percent of the samples collected at each monitoring site are collected as duplicate samples. For each duplicate sampling, two unmarked duplicate samples labeled five minutes apart will be collected from concurrent replicate samples and sent to VDCLS for the purpose of checking the analytical precision of the laboratory.

Field blanks analyzed by VDCLS are used to verify that clean sampling techniques are used by field personnel. Field blanks are collected by processing an analyte-free water through sampling equipment at the field site.

Periodically, standard-reference samples are submitted to VDCLS and the USGS Kentucky Sediment Laboratory in order to check analytical results against a known standard. This allows for determination of the accuracy of each laboratory and the presence of any bias. Sources of reference samples may be either the Environmental Protection Agency or a commercial laboratory.

Completeness is assessed by comparing the number of base flow and stormflow samples completed with those scheduled. The reasons for any discrepancies are well documented.

XIII. CORRECTIVE ACTION FOR OUT-OF-CONTROL SITUATIONS

Out-of-control situations may occur in the field or in the laboratory as a result of equipment breakdown, despite careful planning and attention to procedures.

The primary methods for correcting out-of-control situations in the field are (1) repairing, recalibrating, or adjusting the malfunctioning instruments; or (2) substituting an alternative piece of equipment. Notes are made in the field log books and on the sampling field sheet when out-of-control situations occur. In most instances, no data are lost due to malfunctioning field equipment.

Potential out-of-control situations occurring in the laboratory may be identified by determining constituent concentrations that do not follow established concentration/discharge patterns or that seem out of range. The primary method of correcting out-of-control situations at VDCLS is to first re-examine the paperwork for clerical or translation errors, such as an incorrect date or station. The next step would be to examine the field paperwork to look for any written observations of problems at the site. Finally, if the source of the questionable value could not be discerned, the next step is to contact the laboratory to ask for confirmation of that concentration and to ask for any bench observations that might influence the sample concentrations. Based on the result of any of these steps, any mismatched site information and data would be corrected if possible. No data are ever changed unless there is a logical, fact-based reason for doing so. Any changes and the rationale for the changes are clearly documented on the Field Sheet and initialed by the Project Chief or a senior project person.

XIV. QA REPORTING PROCEDURES

All samples collected will be analyzed at VDCLS in Richmond, VA. VDCLS performance will be evaluated through the use of duplicate and standard-reference samples. Results of the laboratory’s performance will be evaluated annually.

Selected References

Clesceri, L.S., Greenberg, A.E., and Trussell, R.R., eds., 1989, Standard methods for the examination and treatment of water and wastewater (17th ed.), Washington, D.C., p. 2-1š, 5-82.

Cohn, T.A., Delong, L.L., Gilroy, E.J., Hirsch, R.M., and Wells. D.K., 1989, Estimating constituent loads: Water Resources Research, v. 25, no. 5, p. 937-42.

Edwards, T.K., and Glysson, D.G., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments, U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 703 p.

Helsel, D.R., and Cohn, T.A., 1988, Estimation of descriptive statistics for multiply censored water quality data: Water Resources Research, v. 24, no. 12, p. 1997-2004.

Horowitz, A.J., C.R. Demas, K.K. Fitzgerald, T.L. Miller, and D.A. Rickert, 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.

Langland, M.J., Blomquist, J.D., Sprague, L.A., and Edwards, R.E., 1999, Trends and status of flow, nutrients, and sediment for selected nontidal sites in the Chesapeake Bay Watershed, 1985-98: U.S. Geological Survey Open-File Report 99-451, 64 p.

Pettyjohn, W.A., and Henning, R., 1979, Preliminary estimate of ground-water recharge rates, related streamflow and water quality in Ohio: The Ohio State University Department of Geology and Mineralogy Completion Report No. 522, 323 p.

Sholar, C.J. and E.A. Shreve, 1998, Quality-assurance plan for the analysis of fluvial sediment by northeastern region, Kentucky district sediment laboratory: U.S. Geological Survey Open-File Report 98-384, 19 p.

Ward, J.R., and Harr, Albert, 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90-140, 71 p.

White, K.E., and Sloto, R.A., 1990, Base-flow-frequency characteristics of selected Pennsylvania streams: U.S. Geological Survey Water Resources Investigation Report 90-4160, 67 p.

APPENDIX 1 -- EXAMPLE OF FIELD DATA RECORD

Water-Quality Sampling Schedule for Station 01634000 -- **NF Shenandoah River**, 7-1-2006 to 6-30-2007

	FBLNK	SMPL01	SMPL02	SMPL03	CONREP	SMPL04	SMPL05	SMPL06	CONREP	SMPL07	SMPL08	SMPL09	FBLNK	SMPL10	SMPL11	SMPL12	SMPL13	SMPL14	SMPL15	CONREP	SMPL16	SMPL17	SMPL18	SMPL19	CONREP	SMPL20
Gage Height																										
Sample Date																										
Routine Sample																										
Storm Impacted																										
Gage Insp																										
Personnel																										

FBLNK = Field Blank CONREP = Concurrent Replicate

APPENDIX 2 --NATIONAL WATER QUALITY LABORATORY ANALYTICAL REQUEST FORM

U.S. GEOLOGICAL SURVEY – NATIONAL WATER QUALITY LABORATORY
ANALYTICAL SERVICES REQUEST

THIS SECTION MANDATORY FOR SAMPLE LOGIN

NWIS RECORD NUMBER / SAMPLE TRACKING ID	User Code	Project Account	LAB USE ONLY / NWQL LABORATORY ID
	VA	24829QEX1	

STATION ID	Begin Date (YYYYMMDD)	Begin Time	Medium Code	Sample Type
01674500	20		R	7

District Contact Phone Number	End Date (YYYYMMDD)	End Time	District Contact Email
804-261-2634			dlmoyer@usgs.gov

SITE / SAMPLE / SPECIAL PROJECT INFORMATION (Optional)

State	County	Geologic Unit Code	Analysis Status*	Analysis Source*	Hydrologic Condition*	Hydrologic Event*	Chain of Custody	Sample Set
51	101		H	9				

NWQL Proposal Number	NWQL Contact Name	NWQL Contact Email	Program/Project

Station Name: **Mattaponi River near Beulahville, VA** Field ID: _____

Comments to NWQL: **Lab split with VDCLS.**

Hazard (please explain): _____

ANALYTICAL WORK REQUESTS: SCHEDULES AND LAB CODES (CIRCLE A=add D=delete)

SCHED 1: 1161 SCHED 2: 1167 SCHED 3: _____ SCHED 4: _____ SCHED 5: _____ SCHED 6: _____

Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D
Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D
Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D Lab Code: _____ A D

SHIPPING INFORMATION (Please fill in number of containers sent)

___ ALF	___ COD	___ FA	___ FCN	___ IQE	___ IRM	___ RA	___ RU	___ SUR	___ TPCN
___ BGC	___ CRB	___ FAM	1 FU	___ IQL	___ MBAS	___ RAM	___ RUR	1 SUSO	___ UAS
___ C18	___ CU	___ FAR	___ FUS	___ IQM	___ OAG	___ RAR	___ RURCT	___ TBI	1 WCA
___ CC	___ CUR	___ FCA	___ GCC	___ IRE	___ PHE	___ RCB	___ RURCV	___ TBY	___
___ CHY	___ DOC	1 FCC	___ GCV	___ IRL	___ PIC	___ RCN	___ RUS	___ TOC	___

NWQL Login Comments: _____

Collected by: _____ Phone No. _____ Date Shipped: _____

FIELD VALUES

Lab/P Code	Value	Remark	Lab/P Code	Value	Remark	Lab/P Code	Value	Remark
21/00095 Specific Conductance uS/cm @ 25 deg C			51/00400 pH Standard Units			2/39086 Alkalinity – IT mg/L as CaCO3		
/99105	30	split	/			/		

Field Comments: _____

*MANDATORY FOR NWIS

Revised 04/00

APPENDIX 3 -- VIRGINIA DISTRICT OFFICE RIVER INPUT MONITORING FIELD SHEET

THINK TWICE. WORK SAFE. DEPARTMENT OF THE INTERIOR

Version 3: 04/2003

USGS science for a changing world

U. S. GEOLOGICAL SURVEY SURFACE-WATER QUALITY NOTES

NWIS RECORD NO ___ ___ ___ ___ ___ ___ ___ ___

STATION NO. ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ ___ SAMPLE DATE ___ ___/___ ___/___ ___ ___ ___ MEAN SAMPLE TIME(CLOCK) __ __ __ __

STATION NAME _____ SAMPLE MEDIUM _____ SAMPLE TYPE _____ TIME DATUM _____ (eg. EST, EDT, UTC)

PROJECT NO. ___ ___ ___ ___-___ ___ ___ ___ ___ PROJ NAME_____ SAMPLE PURPOSE (71999) ___ PURPOSE OF SITE VISIT (50280) ___

SAMPLING TEAM _____ TEAM LEAD SIGNATURE _____ DATE ___/___/_____

START TIME __ __ __ __ GAGE HT _____ TIME __ __ __ __ GHT _____ TIME __ __ __ __ GHT _____ TIME __ __ __ __ GHT _____ END TIME __ __ __ __ GHT _____

QC SAMPLE COLLECTED? EQUIP BLANK ___ FIELD BLANK ___ SPLIT ___ CONCURRENT___ SEQUENTIAL __ SPIKE ___ TRIP BLANK ___ OTHER ___

NWIS RECORD NOS. _____ _____ _____ _____ _____ _____ _____ _____

LABORATORY INFORMATION

SAMPLES COLLECTED: NUTRIENTS ___ MAJOR IONS ___ TRACE ELEMENTS: FILTERED ___ UNFILTERED ___ MERCURY ___ VOC ___ RADON ___

TPC ___ (VOL FILTERED_____mL) TPC ___ (VOL FILTERED_____mL) PIC ___ (VOL FILTERED_____mL) DOC ___ ORGANICS: FILTERED ___ UNFILTERED ___

ISOTOPES ___ MICROBIOLOGY ____ CHLOROPHYLL ____ BOD ____ COD ____ ALGAE ____ I NVERTEBRATES ____ FISH ____ BED SED. ____

SUSP. SED. ____ CONC. S/F SIZE RADIOCHEMICALS: FILTERED ___ UNFILTERED ___ OTHER _____ OTHER _____

LABORATORY SCHEDULES: _____ _____ _____ _____ _____ _____

LAB CODES: _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE _____ ADD/DELETE

COMMENTS: _____ DATE SHIPPED __ __ /__ __/__ __ __ __

FIELD MEASUREMENTS

GAGE HT (00065) _____ ft

Q, INST. (00061) _____ cfs MEAS. RATING EST.

DIS. OXYGEN (00300) _____mg/L

BAROMETRIC PRES. (00025) _____ mm Hg

DO SAT. (00301) _____ %

eH (00090) _____ mvolts

pH (00400) _____ UNITS

COND (00095) _____ µS/cm@25 °C

TEMP, AIR (00020) _____ °C

TEMP, WATER (00010) _____ °C

TURBIDITY (61028) _____ ntu

ALKALINITY ( ) _____ mg/L

ANC ( ) _____ mg/L

BICARBONATE (00453) _____ mg/L

CARBONATE (00452) _____ mg/L

HYDROXIDE (71834) _____ mg/L

E. COLI ( ) _____ col/100mL

FECAL COLIFORM (31625) _____ col/100mL

TOTAL COLIFORM (31501) _____ col/100 mL

OTHER: _____

OTHER: _____

SAMPLING INFORMATION

Sampler Type (84164) _____ Sampler ID _____ Sample Compositor/Splitter: PLASTIC TEFLON CHURN CONE OTHER _____

Sampler Bottle/Bag Material: PLASTIC TEFLON OTHER _____ Nozzle Material: PLASTIC TEFLON OTHER _____ Nozzle Size: 3/16" 1/4" 5/16"

Stream Width: _____ ft mi Left Bank _____ Right Bank _____ Mean Depth: _____ft Ice Cover _____% Ave. Ice Thickness _____ in.

Sampling Points: _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____

Sampling Location: WADING CABLEWAY BOAT BRIDGE UPSTREAM DOWNSTREAM SIDE OF BRIDGE _____ ft mi above below gage _____

Sampling Site: POOL RIFFLE OPEN CHANNEL BRAIDED BACKWATER Bottom: BEDROCK ROCK COBBLE GRAVEL SAND SILT CONCRETE OTHER _____

Stream Color: BROWN GREEN BLUE GRAY CLEAR OTHER _____ Stream Mixing: WELL-MIXED STRATIFIED POORLY-MIXED UNKNOWN OTHER _____

Weather: ***SKY-*** CLEAR PARTLY CLOUDY CLOUDY ***PRECIP-*** LIGHT MEDIUM HEAVY SNOW RAIN MIST ***WIND-*** CALM LIGHT BREEZE GUSTY WINDY EST. WIND SPEED___

TEMP- VERY COLD WARM HOT ***COMMENTS***_____

Sampling Method (82398): EWI [10] EDI [20] SINGLE VERTICAL [30] MULT VERTICAL [40] OTHER _____ Stage: STABLE, NORMAL STABLE, HIGH RISING FALLING PEAK

OBSERVATIONS: _____

_____

COMPILED BY: _____ **CHECKED BY:** _____ **DATE:** _____

STN NO_____

METER CALIBRATIONS

TEMPERATURE Meter MAKE/MODEL _____ S/N _____ Thermister S/N _____ Thermometer ID _____

Lab Tested against NIST Thermometer/Thermister? N Y Date: ___ ___/___ ___/ ___ ___ ___ ___ **±**_____ °C

Measurement Location: CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4 _____ # 5 _____ **MEDIAN:**_____ **ºC REMARK** ___ ___ **QUALIFIER** ___ ___

pH Meter MAKE/MODEL _____ S/N _____ Electrode No. _____ Type: GEL LIQUID OTHER _____

Sample: FILTERED UNFILTERED CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ FT DEEP VERTICAL AVG. OF _____ POINTS

pH BUFFER	BUFFER TEMP	THEO-RETICAL pH FROM TABLE	pH BEFORE ADJ.	pH AFTER ADJ.	SLOPE	MILLI-VOLTS	BUFFER LOT NO.	BUFFER EXPIRA-TION DATE	COMMENTS
pH 7									
pH 7									
pH 7									
pH ___									
pH ___									
pH ___									
CHECK pH ___									

TEMPERATURE CORRECTION FACTORS FOR BUFFERS APPLIED?

CALIBRATION COMMENTS:

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4_____ # 5 _____ **USE:** _____ **UNITS REMARK** ___ ___ **QUALIFIER** ___ ___

SPECIFIC CONDUCTANCE Meter MAKE/MODEL _____ S/N _____ Sensor Type: DIP CUP FLOW-THRU OTHER_____

Sample: CONE SPLITTER CHURN SPLITTER SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS

Temperature compensation:

AUTO

MANUAL CORR. FACTOR= _____

STD VALUE	STD TEMP	SC BEFORE ADJ.	SC AFTER ADJ.	STD LOT NO	STD EXPIRATION DATE	COMMENTS

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4_____ # 5 _____ **MEDIAN:** _____**µS/cm REMARK** ___ ___ **QUALIFIER** ___ ___

DISSOLVED OXYGEN Meter MAKE/MODEL _____ S/N _____ Probe No. _____

Sample: SINGLE POINT AT _____ ft DEEP VERTICAL AVG. OF _____ POINTS BOD BOTTLE OTHER_____ Stirrer Used? Y N

Air Calibration Chamber in Water___ Air-Saturated Water ___ Air Calibration Chamber in Air ___ Winkler Titration ___ Other_____

Battery Check: REDLINE _____ RANGE _____ THERMISTER Check? Y N _____ Zero DO Check: Y N Solution Date _____

WATER TEMP ºC	BAROMETRIC PRESSURE mm Hg	DO TABLE READING mg/L	SALINITY CORR. FACTOR	DO BEFORE ADJ.	DO AFTER ADJ.

Zero Meter Reading _____mg/lL Adj. to _____ mg/L

Membrane Changed? N Y Date: ____/____/_____ Time: _____

Barometer Calibrated? N Y Date: ____/____/_____ Time: _____

FIELD READING # 1 _____ # 2 _____ # 3 _____ # 4_____ # 5 _____ **MEDIAN:** _____ **mg/L REMARK** ___ ___ **QUALIFIER** ___ ___

STN NO_____

ALKALINITY/ANC CALCULATIONS

BEGINNING H_2O TEMP. _____ °C

pH	ΔpH	VOL ACID DC OR mL	ΔVOL ACID DC / mL	ΔpH / ΔVOL ACID

pH	ΔpH	VOL ACID DC OR mL	ΔVOL ACID DC / mL	ΔpH / ΔVOL ACID

CALCULATIONS

ALKALINITY OR ANC (meq/L) = 1000 (B) (C_a) (CF) / V_s

ALKALINITY (mg/L AS $CaCO_3$) = 50044 (B) (C_a) (CF) / V_s

where:

B = volume of acid titrant added from the initial pH to the bicarbonate equivalence point (near pH 4.5), in milliliters. To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts)

C_a = concentration of acid titrant, in milliequivalents per milliliter (same as equivalents per liter, or *N*)

CF = correction factor (obtain from OWQRL for Hach acid cartridges of certain lot numbers — default value is 1.00)

V_s = volume of sample, in milliliters

For samples with pH ≤ 9.2:

BICARBONATE (meq/L) = 1000 (B-2A) (C_a) (CF) / V_s

BICARBONATE (mg/L) = 61017 (B-2A) (C_a) (CF) / V_s

CARBONATE (meq/L) = 2000 (A) (C_a) (CF) / V_s

CARBONATE (mg/L) = 60009 (A) (C_a) (CF) / V_s

where:

A = volume of acid titrant added from the initial pH to the carbonate equivalence point (near pH 8.3), in milliliters. To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts)

NOTE: For samples with pH > 9.2, these equations for bicarbonate and carbonate will fail to give accurate results. Use the Alkalinity Calculator at http://oregon.usgs.gov/alk

HACH CARTRIDGE CORRECTION FACTOR _____

[SEE QWQRL WEB PAGE (NEWS) FOR INFO]

FIRST TITRATION RESULTS

DATE ___ ___/___ ___/___ ___ ___ ___

TIME ___ ___ ___ ___ TEMP _____

ALKALINITY/ANC _____ meq/L

ALKALINITY/ANC _____ mg/L AS $CaCO_3$

BICARBONATE _____mg/L _____meq/L AS HCO_3^-

CARBONATE _____mg/L _____ meq /L AS CO_3^{2-}

ACID: 1.6N 0.16N 0.01639N

OTHER:_____

ACID LOT NO. _____

ACID EXPIRATION DATE __ __/__ __/__ __ __ __

SAMPLE VOLUME: _____mL

___ FILTERED ___ UNFILTERED

___ INFLECTION POINT TITRATION
___ GRAN METHOD

STIRRING METHOD: ___ MAGNETIC ___ MANUAL

SECOND TITRATION RESULTS

DATE ___ ___/___ ___/___ ___ ___ ___

TIME ___ ___ ___ ___ TEMP _____

ALKALINITY/ANC _____ meq/L

ALKALINITY/ANC _____ mg/L AS $CaCO_3$

BICARBONATE _____mg/L _____meq/L AS HCO_3^-

CARBONATE _____mg/L _____ meq /L AS CO_3^{2-}

ACID: 1.6N 0.16N 0.01639N

OTHER:_____

ACID LOT NO. _____

ACID EXPIRATION DATE __ __/__ __/__ __ __ __

SAMPLE VOLUME: _____mL

___ FILTERED ___ UNFILTERED

___ INFLECTION POINT TITRATION
___ GRAN METHOD

STIRRING METHOD: ___ MAGNETIC ___ MANUAL

COMMENTS/CALCULATIONS:

STN NO_____

MICROBIOLOGY

FECAL COLIFORM

Time collected: __ __ __ __

time in: __ __ __ __ date __/__/_____

time out: __ __ __ __ date __/__/_____

VOLUME mL	COUNT COL/100mL	USED IN CALC?	REMARKS*
BLANK			
BLANK			

INCUBATE 24 hrs @44.5ºC FILTER SIZE=0.7 µM

IDEAL COUNT= 20-60 COL/100mL

RESULT (31625) _____ COL/100 mL

*REMARK ___ ___ **QUALIFIER ___ ___

*REMARKS E=ESTIMATED
<=LESS THAN >=GREATER THAN
**QUALIFIER K=NON-IDEAL COUNT

TOTAL COLIFORM

Time collected: __ __ __ __

time in: __ __ __ __ date __/__/_____

time out: __ __ __ __ date __/__/_____

VOLUME mL	COUNT COL/100mL	USED IN CALC?	REMARKS*
BLANK			
BLANK			

INCUBATE 24 hrs @35 ºC FILTER SIZE=0.45 OR 0.7 µM

IDEAL COUNT= 20-80 COL/100mL

RESULT (31501) _____ COL/100 mL

*REMARK ___ ___ **QUALIFIER ___ ___

*REMARKS E=ESTIMATED
<=LESS THAN >=GREATER THAN
**QUALIFIER K=NON-IDEAL COUNT

E. COLI

Time collected: __ __ __ __

time in at 35ºC: __ __ __ __ date __/__/_____

time in at 44.5ºC: __ __ __ __ date __/__/_____

time out: __ __ __ __ date __/__/_____

VOLUME mL	COUNT COL/100mL	USED IN CALC?	REMARKS*
BLANK			
BLANK			

INCUBATE [SEE NFM] FILTER SIZE=0.45 µM

IDEAL COUNT= [SEE NFM]

RESULT ( ) _____ COL/100 mL

*REMARK ___ ___ **QUALIFIER ___ ___

*REMARKS E=ESTIMATED
<=LESS THAN >=GREATER THAN
**QUALIFIER K=NON-IDEAL COUNT

QUALITY-CONTROL INFORMATION

LOT NUMBERS

PRESERVATIVES 7.5N HNO_3 (FOR METALS&CATIONS) _____ 6N HCl (FOR Hg) _____ 4.5N H_2SO_4 (FOR NUTRIENTS&DOC) _____

1:1 HCL (FOR VOC) _____ CONC. H_2SO_4 (FOR COD, PHENOL, O&G)_____ NaOH (FOR CYANIDE) _____

OTHER _____ _____ _____ **COMMENTS** _____

SPIKE VIALS (99104) _____ _____ _____ **SURROGATE VIALS** _____ _____ _____

BLANK WATER INORGANIC (99200)_____ (992021_____ PESTICIDE (99202)_____ (99203)_____ VOC (99204) _____ (99205)_____

FILTERS CAPSULE_____ PLATE _____ ORGANIC CARBON _____ OTHER _____

CROSS SECTION NOTES

STATION	ft FROM LEFT BANK (00009) OR ft FROM RIGHT BANK (72103)	TIME	DEPTH ft (81903)	DO mg/L (00300)	DO SAT % (00301)	pH units (00400)	Sc µS/cm (00095)	TEMP ºC (00010)	GAGE HT ft (00065)	SUB Q (INST) cfs (00061)	

STN NO_____

OXYGEN DEMAND (BOD) (CBOD)

BLANKS

BOTTLE NO.	INITIAL BOD	DO OR CBOD	5-DAY BOD	DO OR CBOD	BOD	CBOD	AVERAGE BOD	AVERAGE CBOD

RESIDUAL CHLORINE

	positive/ negative	sodium sulfite added	sodium sulfite normality
field test	+ / -		
lab test	+ / -		
After 5-day bod/cbod	+ / -		

SAMPLE

BOTTLE NO.	SAMPLE SIZE DILUTIION	INITIAL BOD	DO OR CBOD	5-DAY BOD	DO OR CBOD	BOD	CBOD

CALCULATIONS

$$BOD_5\ (mg/L) = \frac{D_1 - D_2}{P}$$

where D_1 = initial DO of sample
D_2 = final DO of sample after 5 days, and
P = decimal volumetric fraction of sample used.

COMMENTS_____

_____

_____

DISSOLVED OXYGEN USING WINKLER METHOD

TITRANT: PAO SODIUM THIOSULFATE OTHER _____TITRANT NORMALITY _____N **D.O. =** _____ **mg/L**

FINAL BURETTE READING						
INITIAL BURETTE READING						
mL TITRANT USED						
mL WATER TITRATED						

COMMENTS_____

_____

_____

_____

DISSOLVED OXYGEN (mg/L) = $\left(\frac{200}{\text{mL water titrated}} \right)$ x mL TITRANT x CF*

*APPLY CORRECTION FACTOR (CF) IF TITRANT HAS A NON-STANDARD NORMALITY (STANDARD NORMALITY = 0.025N) CF = NORMALITY OF TITRANT/0.025

TURBIDITY CALIBRATION

Meter: MAKE/MODEL _____ S/N _____ Type: TURBIDIMETER SUBMERSIBLE SPECTROPHOTOMETER

Sample: SAMPLE STORED? Y N HOW LONG? _____

SAMPLE DILUTED? Y N VOL. OF DILUTION WATER _____ mL SAMPLE VOLUME _____ mL

	Date Prepared	Concentration NTU	Temperature °C	Initial instrument reading	Reading after adjustment
Stock Turbidity Standard					
Zero NTU Standard *(DIW)*					
Standard 1					
Standard 2					
Standard 3					

NTU = A x (B+C) / C

A= NTU IN DILUTED SAMPLE
B= VOLUME OF DILUTION WATER, mL
C= SAMPLE VOLUME, mL

COMMENTS_____

_____

_____

_____

_____

FIELD READING #1 _____ #2 _____ #3 _____ #4 _____ #5 _____ **MEDIAN** _____NTU **REMARK** ___ ___ **QUALIFIER** ___ ___

DIGITAL PICTURE OF SITE CAN BE INSERTED HERE

COMMENTS/CALCULATIONS

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

REFERENCE LIST FOR CODES USED ON THIS FORM

Sample Medium Codes
9 Surface water
R Quality-control sample (associated environmental sample –9 (SW))
Q Blanks

Sample Type Code
9 Regular
7 Replicate
2 Blank
1 Spike

Time Datum Codes

Time Zone	Std Time Code	UTC Offset (hours)	Daylight Time Code	UTC Offset (hours)
Hawaii-Aleutian	HST	-10	HDT	-9
Alaska	AKST	-9	AKDT	-8
Pacific	PST	-8	PDT	-7
Mountain	MST	-7	MDT	-6
Central	CST	-6	CDT	-5
Eastern	EST	-5	EDT	-4
Atlantic	AST	-4	ADT	-3

Null-value Qualifiers
e required equipment not functional or available
f sample discarded; improper filter used
o insufficient amount of water

Value Qualifiers
e see field comment
f sample field preparation problem
k counts outside the acceptable range

82398 SAMPLING METHOD
10 Equal Width Increment (Ewi)
20 Equal Discharge Increment (Edi)
25 Timed Sampling Interval
30 Single Vertical
40 Multiple Verticals
50 Point Sample
70 Grab Sample (Dip)
80 Discharge Integrated, Equal Transit Rate (Etr)
90 Discharge Integrated, Centroid
120 Velocity Integrated
8010 Other
8030 Grab Sample At Water-Supply Tap

84164 SAMPLER TYPE
100 Van Dorn Sampler
110 Sewage Sampler
125 Kemmerer Bottle
3039 US D-77 Tm
3040 US D-77 Tm Modified Teflon Bag Sampler
3044 US DH-81
3045 US DH-81 With Teflon Cap And Nozzle
3046 Sampler, D-77 Tm, W/Reynolds Oven Collapsible Bag
3047 Sampler, Frame-Type, Plastic Bottle W/Reynolds Oven Bag
3048 Sampler, Frame-Type, Teflon Bottle
3049 Sampler, Frame-Type, Plastic Bottle
3050 Sampler, Frame-Type, Plastic Bottle W/Teflon Collapsible Bag
3051 US DH-95 Teflon Bottle
3052 US DH-95 Plastic Bottle
3053 US D-95 Teflon Bottle
3054 US D-95 Plastic Bottle
3055 US D-96 Bag Sampler
3060 Weighted-Bottle Sampler
3061 US WBH-96 Weighted-Bottle Sampler
3070 Grab Sample
3080 VOC Hand Sampler
4010 Thief Sampler
4115 Sampler, point, automatic
8000 None
8010 Other

71999 SAMPLE PURPOSE
10 Routine
15 NAWQA
20 NASQAN
30 Benchmark
40 SW Network
60 Lowflow Network
70 Highflow Network
110 Seepage Study
180 Cross-Section Variation

ALKALINITY/ANC PARAMETER CODES
39086 Alkalinity, water, filtered, incremental titration, mg/L
00410 ANC, water, unfiltered, incremental titration, mg/L
29802 Alkalinity, water, filtered, Gran titration, mg/L
29813 ANC, water, unfiltered, Gran titration, mg/L

50280 PURPOSE OF SITE VISIT
1001 Fixed frequency, surface-water
1002 Storm hydrograph, surface-water
1003 Extreme high flow, surface-water
1004 Extreme low flow, surface-water
1005 Diurnal, surface-water
1006 Synoptic, surface-water
1098 NAWQA surface-water quality control
1099 Other, surface-water

3001 NAWQA Occurrence Survey
3002 NAWQA Spatial Distribution Survey
3003 NAWQA Synoptic Study
3098 NAWQA bed-sediment or tissue quality control
3099 Other, bed sediment and tissue

A COMPLETE SET OF FIXED-VALUE CODES CAN BE FOUND ON-LINE AT:
http://wwwnwis.er.usgs.gov/nwisdocs4_3/qw/QW.user.book.html

SAFETY FIRST – EVERY JOB – EVERY TIME

APPENDIX 4 -- STANDARD OPERATING PROCEDURES FOR THE COLLECTION OF FIELD PARAMETERS (pH, Specific Conductance, Dissolved Oxygen, Turbidity, and Temperature) AND CHLOROPHYLL a

pH 6.4

Revised by **George F. Ritz and Jim A. Collins**

Illustrations

Tables

pH 6.4

Revised by **George F. Ritz and Jim A. Collins**

pH is a primary factor governing the chemistry of natural water systems and is measured routinely in U.S. Geological Survey (USGS) studies of water quality. The pH of water directly affects physiological functions of plants and animals and is, therefore, an important indicator of the health of a water system.

pH: A mathematical notation defined as the negative base-ten logarithm of the hydrogen-ion activity, measured in moles per liter of a solution.

The pH of an aqueous system can be understood as an estimation of the activity, or effective concentration,[1] of hydrogen ions (H^+) affecting that system. The theoretical basis of H^+ activity and measurement are described in greater detail in Hem (1989) and in Pankow (1991).

By definition,

$$pH = -log_{10}[H^+], \text{ and}$$

$$[H^+] = 10^{-pH}.$$

- Logarithmic units are used to express H^+ activity because the concentration of H^+ in most environmental waters is usually too low to be expressed as milligrams per liter, micrograms per liter, or moles per liter, in contrast to most other chemical species (Hem, 1989).
- pH is reported on a scale that most commonly is shown to range from 0 to 14 (see TECHNICAL NOTE below). The pH scale is related directly to H^+ and hydroxide (OH^-) concentrations at a given temperature.
  - A solution is defined as having a neutral pH (pH = 7.00 at 25°C) when the H^+ concentration is equal to the OH^- concentration.
  - A solution is defined as acidic if the H^+ activity (concentration) is greater than that of the OH^- ion (pH is less than 7 at 25°C).
  - A solution is defined as basic, or alkaline, when the OH^- concentration is greater than the H^+ concentration (pH is greater than 7 at 25°C).

[1]The majority of natural freshwater systems for which water-quality data are routinely collected by the USGS are considered to be dilute; that is, the volume of dissolved solids is less than 50 milligrams per liter and the ionic strength of the solution (the strength of the electrostatic field caused by the ions) is less than 10^{-4}. For dilute solutions, activity values can be assumed to be equal to measured ion concentrations (Hem, 1989). Therefore, throughout the text of this section, the terms "activity" and "concentration," as they relate to the hydrogen ion, are used interchangeably.

- Temperature affects the chemical equilibria of ionic activities in aqueous solutions, including that of H^+ (Hem, 1989). For example, neutral pH for pure water at 30°C is calculated to be 6.92, whereas at 0°C, neutral pH is 7.48. The pH of pure water at 25°C is defined as 7.00. Therefore, the temperature of the solution must be taken into account when measuring and recording pH.

TECHNICAL NOTE: Although pH commonly is reported on a scale ranging from 0 to 14, pH values of less than 0 can be measured in highly acidic solutions, and pH values greater than 14 can be measured in concentrated base solutions (Nordstrom and Alpers, 1999; Hem, 1989).

6.4.1 EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH consists of a pH meter, sensor(s) (a pH electrode and often a temperature sensor), and buffer solutions (table 6.4–1). Since a variety of instrument systems are available from manufacturers (multiparameter instruments, for example, are described in NFM 6.8), the procedures described in this section may not be applicable or may need to be modified, depending on the specific instrument system being used. Field personnel should:

- Be thoroughly familiar with the information provided in the manufacturer's user manual.
- Adhere to USGS protocols for quality control and assurance of pH measurements.
- Test the meter and electrode before each field trip.

Temperature affects the operation of pH meters, electrodes, and buffer solutions.

Table 6.4–1. Equipment and supplies used for measuring pH[1]

[mL, milliliters; mV, millivolt; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; +, plus: ±, plus or minus; MSDS, Material Safety Data Sheets]

✓	pH meter and pH electrodes Battery powered, solid state, with automatic temperature compensation (for multiparameter instruments, see NFM 6.8) Range of at least 2 to 12 pH, preferably 0 to 14 pH Accuracy of at least ±0.01 units Temperature range of at least 0 to +45°C Millivolt readout with accuracy of ±1.0 mV
✓	pH electrodes, gel-filled or liquid-filled, as appropriate, for study objectives and site conditions
✓	pH electrode filling solution of appropriate composition and molarity (for liquid-filled electrode)
✓	pH electrode storage solution
✓	Thermistor (or thermometer), calibrated
✓	Buffer solutions for pH 4, 7, and 10; temperature correction chart(s) for buffers; labeled with expiration dates
✓	Stand for holding pH electrode
✓	Bottle, delivery (squeeze), to dispense deionized water
✓	Deionized water, maximum conductivity of 1 µS/cm
✓	Beakers or measurement vessels, polyethylene or Teflon® preferable, assorted volumes of 50 to 150 mL, clean but not acid rinsed
✓	Flowthrough chamber (for ground-water measurements)
✓	Minnow bucket (or mesh bag) with tether or equivalent, used for temperature equilibration of buffer solutions
✓	Waste-disposal container
✓	pH-meter/electrode logbook for recording calibrations, maintenance, and repairs
✓	MSDS for all pH buffers and other reagents to be used

[1]This list pertains to single-parameter instruments for measuring pH. Refer to NFM 6.8 for information on and general use of multiparameter instruments. This list may be modified to meet the specific needs of the field effort.

CAUTION: Keep Material Safety Data Sheets (MSDS) readily available and refer to them to ensure that pH buffers or other chemicals are handled safely.

6.4.1.A pH METERS

A pH meter is a high-impedance voltmeter that measures the very small, direct current potential (in millivolts (mV)) generated between a glass pH electrode and a pH reference electrode. The potentiometric measurement is displayed as a pH value. The meter uses potentiometric differences to generate these pH values and is programmed with (1) the ideal Nernstian response relating hydrogen-ion activity (concentration) and electrical response (59.16 mV/unit pH), and (2) an automatic temperature compensation (ATC) factor. Since the ideal Nernstian slope response from the electrode varies with temperature, the meter's software adjusts the slope to be in accordance with the Nernst equation at the corresponding environmental temperature during calibration and measurement (refer to section 6.4.3 for an explanation of the Nernst equation).

6.4.1.B pH ELECTRODES

The pH electrode is a special type of ion selective electrode (ISE) that is designed specifically for the measurement of hydrogen-ion concentration in a dilute aqueous solution.

- Diodes or triodes (combination electrodes) are used in most USGS field studies.
  - Combination electrodes are housed either in a glass or an epoxy body. Diodes contain a pH reference electrode and pH measurement electrode. Triodes contain the reference and measurement electrodes plus a thermistor. In either case, the basic electrode operation is the same (IC Controls, 2005a).
  - All combination pH electrodes have a glass membrane, a reference and a measurement electrode, an ionic (filling) solution, and a reference junction (shown on fig. 6.4–1); these are described below.

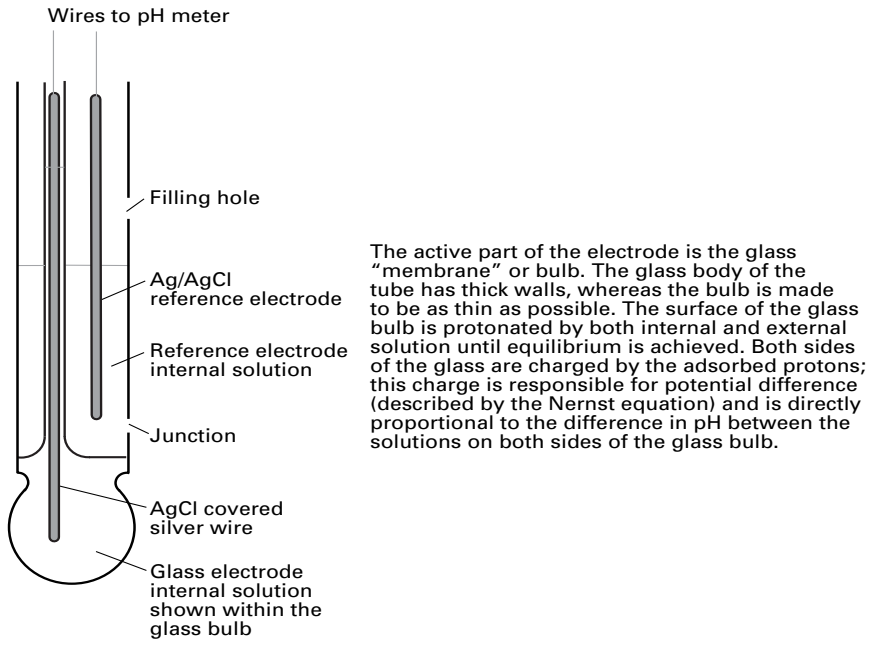


Figure 6.4–1. Diagram of a combination (single-junction) pH electrode. Modified from pH-meter.info (2005).

- Electrode performance naturally degrades over time with normal use. However, field personnel need to be alert to those chemical environments that can cause serious and more rapid degradation of electrode performance (IC Controls, 2005a). Many such environments are coincident with industrial, mined, and urban areas (table 6.4–2).
  - Field personnel should be aware of the effect on the pH measurement when deploying the electrode in such environments: document field conditions on field forms.
  - When measuring pH under specific adverse chemical conditions, the use of electrodes with properties designed to withstand such conditions is recommended (table 6.4–2).

Table 6.4–2. pH electrodes recommended for water having elevated concentrations of sodium and other monovalent major cations, sulfide, cyanide, and ferric chloride.

[H^+, hydrogen ion; Na^+, sodium ion; >, greater than; ≥, greater than or equal to]

Chemical condition	Description of water	Degradation effect on a common combination pH electrode	Recommended pH electrode
Basic ions dominant in solution	pH high (>10 pH units); low H^+ activity results in measurement of other monovalent ions in solution.	Sluggish response to changes in pH, resulting from dehydration of the glass membrane.	Glass pH electrode designed for measuring high values of pH.
	Sodium effect: Elevated Na^+ at pH ≥11.0, H^+ activity is low. The electrode senses Na^+ activity as if it were H^+ because of the similar charge and structure of the Na^+ and H^+ ions.	The pH measurement is negatively biased.	Glass pH electrode designed for measuring high values of pH.
Elevated concentrations of sulfide or cyanide	Elevated concentrations of sulfides or cyanides are found in industrial, mined, or urban areas.	Sulfide or cyanide contamination of the internal reference electrode.	Double-junction electrodes and plasticized reference electrodes.
Elevated concentration of ferric chloride	Ferric chloride is used as a flocculating agent in wastewater treatment plants, for example.	Ferric chloride attacks the glass membrane of the pH electrode, deactivating many of the sensing sites on the glass surface.	Consult the manufacturer for (1) selecting pH electrodes that can withstand this environment; and (or) (2) specific cleaning procedures for the glass membrane.

Glass membrane. The most essential and vulnerable element of the pH electrode is the sensitive glass membrane, which permits the sensing of hydrogen-ion activity in most natural waters. When the pH electrode is immersed in a solution (for example, a calibration buffer or a sample solution), ions from the glass diffuse into a thin layer on the outside of the membrane, while hydrogen ions diffuse through this layer until an equilibrium is reached between the internal and external ionic concentrations. In this way, an electrical potential is developed across the sensing surface, which is proportional to the concentration of hydrogen ions in the surrounding solution (pH-meter.info, 2005).

A clean, undamaged glass membrane is necessary for performing an accurate measurement of pH.

Reference and measurement electrodes. Contained within the pH-sensor body are a reference electrode (that generates a constant electrical potential) and a pH-measurement electrode. The measurement electrode generates a separate electrical potential that is proportional to the concentration of hydrogen ions in the sample solution. The electrodes together form a complete electrical circuit; when the diffusion of hydrogen ions reaches equilibrium, no electrical current is present, and the difference in electrical potential that exists between the reference and the measurement electrodes is an indication of the hydrogen-ion concentration in the solution. The pH meter, sensing this minute difference in electrical potentials, converts this difference into a pH value based on the latest calibration of the pH electrode.

Ionic (filling) solutions. An ionic solution used to fill the space within the pH electrode is the source of mobile, chemical ions that serve to complete the electrical circuit between the internal reference and pH-measurement electrodes.The pH electrode may be filled either with an ionic liquid solution (liquid-filled pH electrode) or an ionic gel solution (gel-filled pH electrode). Typically, these ionic solutions contain a chloride salt (usually silver or potassium) of a known and specific molarity (strength). For liquid-filled electrodes, maintaining a sufficient volume and the correct molarity of the filling solution within the electrode is very important to achieving meaningful measurements. Most standard pH electrodes are designed to function well when the electrode filling solution strength is similar to the sample ionic strength, typically having a relatively high ionic strength of 3 molar (M) or greater. Using low ionic-strength or high ionic-strength pH electrodes and a filling solution of appropriate composition and molarity—as recommended by the electrode manufacturer—is recommended when working with environmental samples having conductivities less than 100 µS/cm or greater than 20,000 µS/cm, respectively.

Reference junction. The liquid reference junction (sometimes called the "salt bridge") is an electrically conductive bridge within the pH electrode, between the reference ionic solution and the sample being measured. This junction is necessary for the proper functioning of the pH-sensing electrical cell; it must allow free movement of electrons, but at the same time, isolate the ionic solution from the bulk environmental sample. Typically, this junction is made of a porous material such as ceramic, Teflon, or glass fiber, and may clog and malfunction if not maintained properly. The function of the reference junction is characterized by a chemical memory. In a correctly functioning pH electrode, a small amount of time lapses before the appropriate ionic bridge is formed between the electrode reference ionic solution and the external environmental sample or external calibration-buffer solution. The length of time necessary for the establishment of this ionic equilibrium is a primary reason for the requirement that pH be measured in a quiescent sample solution. (Sections 6.4.4 and 6.4.5 provide further discussion.)

Remember to check that the junction on the pH electrode is not clogged; a clogged electrode will not function properly.

Electrode performance naturally deteriorates over time under normal operating conditions. However, use of the electrode in severe chemical environments can cause more rapid deterioration (table 6.4–2). Many of these environments are coincident with industrial and urban locations: immersing a pH electrode in such environments should be avoided or minimized to the extent possible (IC Controls, 2005a). Whenever the pH electrode is exposed to conditions such as those listed on table 6.4–2, this information should be recorded in the pH-meter/electrode logbook and documented in field notes.

pH BUFFER SOLUTIONS 6.4.1.C

pH buffer solutions (buffers) are ionic solutions that are used to calibrate the pH instrument system. Buffers maintain constant pH values because of their ability to resist changes to the specific pH value for which they are produced. **Measurements of pH are only as accurate as the buffers used to calibrate the electrode.**

- Use only buffers that have been certified traceable to an NIST standard reference material.
- Select the buffer molarity that is appropriate for the ionic strength of the water to be measured and the instrument system that will be used.
  - For pH measurements of dilute waters with conductivities less than 100 µS/cm, use of buffers having lower-than-standard molarity and a low ionic-strength pH electrode is recommended (refer to section 6.4.3.B).
  - For pH measurements in high ionic-strength waters with conductivities greater than 20,000 µS/cm, use of buffers having a higher-than-standard molarity is recommended (refer to section 6.4.3.C).
- Label pH buffer containers with the acquisition date and the expiration date. Copy the expiration date and the buffer lot number onto any reagent containers into which the buffer is transferred. Copy the temperature-correction information onto the respective buffer container or keep a copy of this information with the buffers being transported to the field.
- **Discard the pH buffer on its expiration date**. The pH of a buffer can be altered substantially because of temperature fluctuation, carbon dioxide (CO_2) absorption, mold growth, or evaporation.

Use the following precautions and protocols to help ensure the accuracy of the pH measurement *(modified from Busenberg and Plummer, 1987):*

- Cap buffer bottles firmly after use to prevent evaporation and contamination from atmospheric CO_2. The pH 10 buffer has the greatest sensitivity to CO_2 contamination, whereas the pH 4 buffer is the least sensitive. Buffers are stable for the short exposure time during electrode calibration.
- Never pour used buffer back into a bottle containing the stock buffer solution.
- Do not insert an electrode or other material into a bottle containing stock buffer solution — **always pour the buffer into a separate container** and discard the solution after use.
- Take care not to contaminate the buffer with another buffer or with other fluids.
- **Do not let the buffer become diluted** (this can happen, for example, if deionized water used to clean the electrode drips into the buffer).
- **Protect buffers against wide temperature variations**, whether in transit, during use, or in storage. Never expose buffers to extreme heat or freezing temperatures. If buffers experience these conditions, their pH values can no longer be assumed to be valid. Discard buffer solutions and any other reagents appropriately.
- Before using buffers in the calibration sequence, bring them to the temperature of the sample solution as much as possible. Since buffer composition differs among manufacturers; check the temperature-correction factors provided by the manufacturer in order to assign the correct pH value to the buffer for the temperature of the buffer at the time of calibration.

In order of greatest to least sensitivity of standard buffers to CO_2 contamination: pH 10 buffer > pH 7 buffer > pH 4 buffer. In order of greatest to least variation of buffer pH with change in temperature: pH 10 buffer > pH 7 buffer > pH 4 buffer.

6.4.2 MAINTENANCE OF pH INSTRUMENTS

Proper care of pH meters, and particularly of the electrode, is essential for maintaining the accuracy and precision required for pH measurements and promotes the longevity of the equipment. pH instrument maintenance includes adhering to the manufacturer's instructions for the use and care of the instrument, and routine use of appropriate electrode cleaning, reconditioning, and storage requirements. As always, follow the manufacturer's instructions for the specific type of electrode in use.

Electrode performance must be monitored before every water-quality field trip and again while at the field site.

6.4.2.A ELECTRODE CARE AND CLEANING

USGS field personnel should integrate the following guidance for the care and cleaning of pH electrodes into their routine field-measurement procedures.

- Never handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with the design characteristics of the glass membrane and affect subsequent pH measurements.
- Inspect the electrode and electrode cable for physical damage. For example, check for
  - Cut or frayed cable(s).
  - Broken connectors and mismatched or missing parts.
  - A visibly scratched or broken bulb, cracked electrode body, and broken or damaged internal electrode (reference and measurement electrodes).
- Gel-filled electrodes do not require filling and typically require less maintenance than liquid-filled electrodes. Do not store gel-filled electrodes in dilute water, even temporarily, as salts may leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.

To prepare and care for liquid-filled electrodes:

1. Remove salt crystal deposits from the electrode, membranes, and junctions by rinsing with deionized water (DIW). Visually check that the reference junction is not blocked or caked with salt. Thorough rinsing with DIW should remove these deposits. Be sure to unplug the fill hole before making pH measurements, as suction pressure may affect the proper movement of ions in the filling solution and the correct operation of the reference junction. Re-plug the fill hole after use.
   - If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the electrode in the air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet the junction.
   - After 15 minutes, visually inspect the junction for liquid or new salt accumulation. Ensure that the filling solution is flowing freely. Refer to the manufacturer's instructions.
2. Check the filling solution level and replenish it if necessary. The solution should reach the bottom of the fill hole. **Filling solutions differ in molarity and composition—always check that the correct filling solution required by the manufacturer for a particular electrode is being used.**
3. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (check the manufacturer's recommendations).
4. Keep a record of the electrode and meter operation and maintenance and repairs in the pH-meter/electrode logbook.
   - Record in the calibration logbook the operational history of each pH electrode.
   - Record the Nernst slope reading and the millivolt readings at pH 4, 7, 10, or other pertinent pH buffer values (based on field study objectives) during calibration. Properly working electrodes should give 95 to 102 percent response of that expected from the theoretical Nernst relationship (Busenberg and Plummer, 1987).

     TECHNICAL NOTE: The theoretical Nernst response is 59.16 mV/pH unit at 25°C, but varies based on temperature. Adequate adjustment of the Nernstian relation requires manual or automatic temperature compensation (ATC). Most modern pH meters have the ATC feature. A slope of 95 percent or less signals probable electrode deterioration and the need to monitor closely any further decline in slope percent. Consider replacing the electrode if calibration slope values cannot be brought to greater than 95 percent. **Do not use an electrode with a slope of less than 95 percent.**
5. Keep the electrode bulb moist and capped when not in use. Use only the wetting solution recommended by the manufacturer.

For routine cleaning of the pH electrode:

Keeping electrodes clean and the liquid junction free-flowing is necessary for producing accurate pH measurements. Because of the variety of electrodes available, check the manufacturer's instructions for specific tips and precautions.

1. **Before and after each use—**rinse the electrode body thoroughly, using only DIW. Dispense the DIW from a squeeze bottle.
2. Do not wipe or wick moisture from electrodes with paper towels or ChemWipes® as these can scratch the pH glass membrane. Wiping the electrode body with paper also may cause a static charge (polarization) on the exterior of the pH electrode, which can also adversely affect the pH measurement.

6.4.2.B RECONDITIONING OF LIQUID-FILLED ELECTRODES

If problems persist during calibration of a liquid-filled electrode, or if there is reason to doubt that the electrode is in good working condition, check the manufacturer's instructions for how to test and recondition the electrode. Reconditioning procedures should be implemented only if the electrode's slope response has deteriorated to less than 95 percent. Document in the pH-meter/electrode logbook if the electrode has been reconditioned or replaced.

The following general procedures can be used to attempt to bring the liquid-filled electrode back into proper working condition:

1. Remove the old filling solution from the electrode.
   a. Place the needle of a 1- or 3-milliliter (mL) syringe into the electrode filling hole (or use other methods of removing the filling solution, such as vacuum extraction or draining).
   b. Tilt the pH electrode until the filling solution is near the fill hole and the needle tip is covered with the filling solution.
   c. Pull back on the syringe plunger until the syringe is full.
   d. Discharge the solution from the syringe into a waste container and repeat steps 1(a) through (d) until all of the filling solution has been removed from the pH electrode.
2. Flush the pH electrode with DIW.
   a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with DIW.
   b. With a syringe, remove the DIW from the pH electrode chamber.
   c. As a result of changes in pressure, temperature, and evaporation, visible crystals may form in the pH electrode. If these are present, continue to flush with DIW until all the crystals have been dissolved and removed from the pH electrode.
3. Fill the electrode with fresh filling solution. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.
   a. Partially fill the pH electrode chamber with the filling solution.
   b. Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.
   c. Remove and discard the filling solution to a waste container.
   d. Refill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. **Be sure to use the appropriate type and molarity of filling solution.**
   e. Rinse any excess filling solution from the outside of the electrode with DIW.
4. After following the reconditioning procedures, retest the electrode**. If the procedures fail to remedy the problem, discard the electrode.**

ELECTRODE STORAGE 6.4.2.C

Electrodes must be clean before they are stored for any length of time. Refer to the manufacturer's instructions for the proper short-term (used daily or weekly) and long-term (2 to 4 months) storage requirements of the electrode.

General guidelines for short-term storage:

1. Storage solutions are specific to the type of electrode; check the manufacturer's manual for each electrode. **Do not store glass hydrogen-ion electrodes in DIW** unless instructed to do so by the manufacturer.
2. Storage solutions have a limited shelf life. Label storage solution containers with the expiration date and discard expired solutions on that date and in a proper manner.
3. Do not place a small piece of cotton or paper towel in the electrode cap to help keep it moist, as this can scratch the glass membrane sensor.
4. Store liquid-filled pH electrodes upright.
5. Store liquid-filled electrodes wet between uses to maximize their accuracy and response time.
   - The glass membrane (bulb) should be fully immersed in the proper electrode storage solution.
   - Between field sites, replace the plug on the fill hole and cover the electrode bulb with the cap.
   - Fill the cap with enough storage solution to keep the bulb wet.
6. Gel-filled electrodes should be stored according to the manufacturer's instructions.

General guidelines for long-term storage:

1. Liquid-filled electrodes may need to be drained of filling solution; follow the manufacturer's instructions.
2. Clean the electrode contacts and connector (with alcohol, if necessary). Allow the contacts to dry and seal and store them in a plastic bag.
3. Store every component of the pH measuring system in an area that is clean, dry, and protected from extremely hot or cold temperatures.

6.4.3 CALIBRATION OF THE pH INSTRUMENT SYSTEM

Proper calibration of the pH instrument system is crucial to accurate pH measurement of environmental samples. During calibration, the pH electrodes are immersed in buffer solutions of known pH (section 6.4.1.C). The buffers are designed to produce a corresponding electrical response potential (usually in millivolts) for the specific pH buffer (for example, pH = 4, 7, or 10 buffer solution) within the pH electrode. These potentials are measured by the pH meter. The Nernst equation gives the expected (theoretical) response potential of the pH buffer at the specific temperature of the calibration (Hem, 1989; see TECHNICAL NOTE below). Note that the measured temperature must be programmed into the pH meter unless the meter has incorporated automatic temperature compensation. The calibration returns the actual, measured potential.

TECHNICAL NOTE: pH electrodes operate on the principle that differing concentrations of the H^+, in buffers or environmental samples, produce differing potentiometric responses (measured in millivolts). The Nernst equation is used to establish the calibration of the pH instrument system by determining the slope of electrical potential versus pH at a given temperature. At 25^0C, this Nernstian relation (the slope along any two points on the line plotted for electrical potential versus pH) is known to be 59.16 mV/pH units. To calculate the slope between two points along the line of measured potentials versus pH:

$$E=E^0- S(pH)$$

where

S = slope

E = electrode pair potential, in mV, and

E^0 = standard potential, in mV.

Thus, using two buffers of known pH (pH_1 and pH_2),

$$E_1=E^0- S(pH_1) \quad and \quad E_2=E^0- S(pH_2).$$

Rearrange as:

$$s = \frac{E_2 - E_1}{pH_1 - pH_2}$$

The theoretical slope is temperature dependent; the theoretical slope (in mV) can be calculated as:

$$S_t=0.19841(273.15 + t)$$

where

t = temperature in degrees Celsius, and

S_t = slope at a given temperature.

The primary concept in accurate calibration of the pH electrode is to select pH buffers with values that bracket the expected pH of the environmental sample; this is known as a two-point calibration. Before field calibration of the pH instrument system, it is useful to estimate (or to anticipate from historical site data, if available) the pH and conductivity of the waters to be encountered at the field sites. If no data are available from which to estimate sample pH, then pH indicator paper can be used onsite as a gross indicator of the pH of the system. (**Under no circumstances should a pH value from indicator paper be recorded as site pH.)** For three-point or other multipoint calibrations, follow the manufacturer's instructions for (a) which buffers to use and (b) the sequence of buffer use.

> **EXAMPLE:** When measuring pH in a stream that is within the normal range of specific electrical conductivity,
>
> a. If pH values are expected to be between 7 and 8, then the standard pH 7 and pH 10 buffers should be selected.
>
> b. If pH values are expected to be less than 7, then the standard pH 7 and pH 4 buffers should be selected.
>
> c. If the anticipated pH range in pH is large, a check of electrode performance using a third standard buffer value is advisable.

The following guidelines and standard procedures apply in general whenever a pH instrument system is to be calibrated. Because calibration and operating procedures can differ with differing instrument systems, check the manufacturer's recommended calibration procedures and calibration solutions. Digital pH meters automatically compensate for buffer temperatures and indicate appropriate Nernst values (in millivolts). When using these instruments, follow the manufacturer's calibration instructions precisely—**do not take shortcuts**.

- Before each field trip and field calibration, check pH meter/electrode logbook records for electrode performance. **Remember—**any noted calibration slope of 95 percent or less indicates probable electrode deterioration; at 94-percent slope or less, the electrode should not be used.
- Use at least two pH buffer solutions of documented, traceable pH value for adequate calibration of the pH instrument system.
- Pour the amount needed of each buffer from the source container into a clean, polyethylene bottle dedicated for the respective buffer, and label the bottle with the buffer's pH value, lot number, expiration date, and the temperature-adjusted pH values provided by the manufacturer for that buffer.
- The temperature of the buffer solutions should be near the same temperature as the water to be sampled. A calibration check of the temperature sensor must be performed at least annually (NFM 6.1).

> **TECHNICAL NOTE:** Temperature has two effects on the pH measurement of a sample—temperature can affect meter and electrode potentials (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect) within the sample. The electrode-potential problem can be solved by using an automatic or manual temperature compensator. The change in hydrogen-ion activity resulting from temperature changes in the sample will be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

Do not use pH buffers that have exceeded their date of expiration.

6.4.3.A CALIBRATION PROCEDURE UNDER STANDARD AQUEOUS CONDITIONS

"Standard aqueous conditions" refers to environmental water with an ionic strength that is within the range in which a standard buffer solution and combination pH electrode can be appropriately used to achieve an accurate pH measurement. For routine USGS water-quality measurements, ionic strengths ranging from 100 to 20,000 μS/cm are considered standard.

When calibrating the pH electrode:

1. Bring the pH buffers to the ambient temperature of the stream or ground water to be measured, to the degree possible under the prevailing field conditions. The temperature sensor (liquid-in-glass or thermistor thermometer), measurement vessel, and electrode also should be at or near the ambient temperature of the environmental sample. **Maintain each buffer as close to sample temperature as possible when calibrating the electrode.**
   - Surface water and ground water—When equilibrating the buffer temperature to ambient surface-water temperature, one method is to place the buffer bottles in a minnow bucket or mesh bag and suspend them in the body of surface water. Alternatively, place the buffers into a bucket or insulated cooler (a) containing surface water, or (b) being filled with ground water.
   - **When immersing buffer bottles in water, ensure that the bottle is firmly capped and that the water level remains below the cap so that water cannot enter the bottle and contaminate the buffer**.
2. Inspect the pH electrode.
   a. Check for damage to the electrode bulb, body, or cables.
   b. Rinse any mineral precipitate off the electrode with DIW.
   c. Uncover (unplug) the fill hole.
   d. If you can visually see small bubbles within the electrode solution, **gently** tap the electrode body to dislodge them. Bubbles trapped in the sensing tip of the electrode will affect the physical conditions necessary for correct operation of the electrode. **Do not wipe moisture from the electrode.**
3. Power up the pH meter. The meter will perform an internal self-test. Note any discrepancies displayed by the meter and record these in the pH-meter/electrode logbook. Malfunctioning meters usually require manufacturer attention; do not try to fix malfunctioning meters in the field. Having backup meters for field trips is necessary for this reason.
4. Record in the ph-meter/instrument logbook the internal self-test information displayed by the pH meter. A calibration log is **mandatory** for all calibrations.

5. Initiate the calibration process by pushing the required calibration display sequences for the particular pH meter and electrode. **Standard USGS procedure for calibration of a single-parameter pH meter-and-electrode system requires a two- or three-point calibration.**
   - Some types of pH-instrument systems may use a different multipoint calibration procedure; in such cases, follow the instructions provided in the instrument manual.
   - A single-point calibration, recommended by some manufacturers, is not acceptable for USGS field measurement of pH.
6. Record in the pH-meter/electrode logbook: pH value, measured temperature, lot number, and expiration date of the first buffer. Typically, the meter will initially indicate the pH 7 buffer (isoelectric point).
7. Begin calibration procedures:
   a. Note that the electrode and thermistor must be rinsed with DIW at least three times between uses of each buffer.
   b. Rinse the electrode twice with the first buffer (usually the pH 7 buffer). Do not allow the glass membrane of the electrode to come in contact with the sides or bottom of the beaker or other measurement vessel.
      i. **First rinse—**Pour enough buffer into a small beaker or other vessel so that it covers the electrode reference junction; swirl the buffer to rinse the electrode body from above the reference junction to the bottom of the bulb. Discard buffer appropriately.

      ii. **Second rinse—**Pour the next aliquot of buffer into the vessel and immerse the electrode in the buffer for 1 minute. Discard buffer appropriately.
   c. Pour another aliquot of buffer into the vessel. Immerse the electrode for 1 minute, without swirling the buffer solution.
   d. Record the pH measurement shown on the meter display in the pH meter/electrode logbook, along with the buffer temperature reading and the pH value from the buffer and temperature table.
      - For pH meters displaying millivolt values, the meter will display the value associated with the pH 7 buffer, as compensated for the buffer temperature.
      - **For properly functioning electrodes, the pH 7 millivolt value should be between +10 and -10 mV. Record the millivolt data in the pH-meter/electrode logbook.**
   e. Press "Cal" or other display instructions to lock in the pH 7 calibration.

> **TECHNICAL NOTE:** During the calibration sequence, after the DIW and buffer rinses and when the specific buffer value is ready to be locked in to the calibration, some meters provide the opportunity to adjust the initially displayed pH value to a corrected pH value for that buffer solution.
>
> - **If this adjustment is equal to or less than 0.05 pH units**, proceed with the adjustment, but specifically note this in the pH meter/electrode logbook.
>
> - **If the adjustment would exceed 0.05 pH units**, the pH electrode is not functioning optimally; consider reconditioning the electrode or using another electrode until the cause of the substandard performance can be determined.

8. **Return to step 6 above, followed by step 7**, repeating each of the procedures just followed but using either the pH 4 or pH 10 buffer, whichever buffer solution, along with the pH 7 buffer, brackets the pH values of the environmental water to be sampled. Record all the calibration data, including the millivolt data, in the pH meter/electrode logbook (see step 7 to test the adequacy of the calibration using the slope test or millivolt test).

9. **At this point, the electrode should be calibrated**. Check the adequacy of the calibration and that the electrode is functioning properly, using the slope test or (and) the millivolt test. Some instruments have the capability to display the slope value; this datum should be recorded in the pH-meter/electrode logbook.

   - **The slope test.** Values ranging from 95 to 102 percent slope are acceptable—if the slope-percent value is outside of this range: clean the electrode and check the level of the filling solution, that the fill hole is open, and that the junction is free-flowing; then, recalibrate.

     TECHNICAL NOTE: Since the theoretical Nernstian relation between electrical response and pH at the calibration temperature is programmed into the pH meter software, the calibration process provides the Nernstian response from the electrode/meter system being calibrated. The actual calibration slope is calculated and the **displayed slope value** represents the actual slope of the electrical potential (millivolt)– pH line that this calibration has produced.

   - **The millivolt test.** For pH meters that display and store only millivolt readings (do not display the slope percent), use the following guidelines to ascertain adequate calibration:
     - pH 7 buffer: Displays between -10 to +10 mV
     - pH 4 buffer: Displays between +165 to +195 mV
     - pH 10 buffer: Displays between -165 to -195 mV
   - If using buffers other than the standard pH 4, 7, and 10 buffers, refer to the information provided with the specific buffer lot to determine the correct, temperature-compensated millivolt potential for that buffer.

10. **Replace the electrode** if, after recalibration, the slope remains outside the acceptable range of 95 to 102 percent or if the acceptable range of the millivolt response is not met at any of the calibration points.

CALIBRATION FOR LOW IONIC-STRENGTH WATER 6.4.3.B

Calibration of pH instrument systems with standard buffers does not guarantee accurate and (or) timely pH measurement in low ionic-strength waters (conductivity less than 100 µS/cm) and in very low ionic-strength waters (conductivity less than 50 µS/cm). As sample ionic strength decreases, the efficiency of the standard pH instrument system also decreases. Low or very low ionic-strength waters have little buffering capacity and may readily absorb atmospheric CO_2, resulting in the formation of carbonic acid in the sample. A continuous change in pH values can occur from the varying reaction rates of the sample water with CO_2, resulting in an unstable measurement.

Standard pH electrodes do not respond well in waters with low ionic strength.

- Standard combination pH electrodes respond more slowly, the response is characterized by continual drift, and calibration is difficult to maintain. Equilibration with the sample water may not be completely achieved or the equilibration time may be on the order of hours.
- Standard pH electrodes exhibit a jumpy response and are more sensitive to conditions of flow and agitation, and measurement accuracy decreases (Wood, 1981).

When preparing to measure pH in low ionic-strength waters, the response time, accuracy, and reproducibility of the measurement can be improved by modifying the type of electrode and buffer.

To measure pH in water of low ionic strength:

1. Use a specific, low ionic-strength electrode. The pH electrode for low ionic-strength solutions typically is characterized by
   - A thin, responsive glass membrane;
   - A reference junction that allows rapid electrolyte flow; and
   - A pH-neutral ionic additive within the reference filling solution.
2. Use corresponding low ionic-strength pH buffers.
   - The low ionic-strength buffer should contain the same type of pH-neutral ionic additive as that in the electrode reference filling solution (the amount of pH neutral ionic additive must be the same in the electrode and buffer, so that the net pH effect is standardized).
   - Low ionic-strength buffers may not be of the standard pH buffer values (pH = 4, 7, 10). Check that your pH meter can accept these “nonstandard” buffer values for calibration.

Calibration of the pH instrument system and measurements made in low ionic-strength solutions should involve a specific combination of low ionic-strength buffers and low ionic-strength electrodes.

6.4.3.C CALIBRATION FOR HIGH IONIC-STRENGTH WATER

USGS studies increasingly involve pH measurement and sampling of high ionic-strength waters (ionic strength greater than 3 *M* or conductivity greater than 20,000 µS/cm) from sources such as industrial effluent (for example, from paper mills, oil refineries, carbonate processing or other mining activities that have corrosive properties), combined sewer/storm water from urban systems, seawater, and brines. Using standard buffers or standard equipment may not yield an accurate pH measurement for such waters.

- The high ionic strength of some industrial effluents or brines often are of greater or equal ionic strength than that of the filling solution in the standard pH electrode. This results in an ionic gradient toward the reference junction and into the pH electrode, which compromises the design parameters of the electrode and therefore the soundness of the calibration and the pH measurement.
- Standard buffers are not of an ionic strength that approximates or exceeds the ionic strength of the sample solution, and standard filling solutions in pH electrodes similarly may have too low of an ionic strength to be calibrated properly for measurement of pH in high ionic-strength waters.

When selecting the measurement system to be used to determine the pH of high ionic-strength waters, consider the following options:

1. Obtain high ionic-strength (conductivity greater than 20,000 µS/cm) pH buffer solutions from commercial sources, if available. Follow the guidelines for maintenance and use of pH buffers previously described in section 6.4.1.C, paying close attention to the effect of temperature on buffer values.
2. Obtain high ionic-strength pH glass electrodes, if available. These may be characterized by filling solutions of greater than 3 *M* ionic strength and more solution-specific glass sensors. Note specific uses recommended by the manufacturer and follow the manufacturer's instructions.
3. If no suitable pH glass electrode/buffer system is available for pH measurement in high ionic-strength environments, investigate the suitability of alternative instrumentation and methods, such as those that employ spectrophotometric or optical methods, with respect to the site-specific conditions to be encountered and study data-quality objectives (Bellerby and others, 1995; Farquharson and others, 1992; Sedjil and Lu, 1998).
    - Spectrophotometric methods typically involve the constant-rate introduction of acid-base indicator dyes into the sample; pH measurement is accomplished by measurement of the resultant spectra of the dye. An important limitation to this system is that acid-base indicator dyes are typically sensitive over very narrow pH ranges (Raghuraman and others, 2006).
    - Spectrophotometric measurement of pH in environmental samples is a methodology designed for specific environments; follow the guidelines provided by the equipment manufacturer.
    - As part of USGS studies, any pH data obtained by spectrophotometry or other nontraditional pH measurement method must be entered under the unique parameter and (or) method code designated in the USGS National Water Information System (NWIS) water-quality database.

CALIBRATION FOR THE pH SENSOR IN MULTIPARAMETER INSTRUMENTS 6.4.3.D

Before beginning calibration of the pH electrode in a multiparameter instrument sonde, read and follow carefully the instrument manual and manufacturer's instructions. Guidelines that incorporate USGS protocols for pH calibration and measurement are described in NFM 6.8.

General procedures for calibration of the pH sensor in a multiparameter sonde:

1. Select the pH 7 and one additional buffer solution that will bracket the anticipated pH of the sample. Equilibrate the temperature of the buffers to the temperature of the environmental sample.
2. Rinse the sonde and electrode thoroughly three times with DIW before and between use of each buffer solution.
3. Rinse the pH and temperature sensors three times with separate aliquots of the first pH buffer, using the "pour-swirl-discard, pour-sit-discard, pour-sit-measure" method described in section 6.4.3.A. Allow enough time for the sensors to equilibrate to buffer temperature before locking in the first calibration point.
4. Repeat step 3, using the second pH buffer, and lock in the second calibration point. (Depending on site conditions and study objectives, it might be useful to check the calibration range of the pH sensor using a third buffer; if appropriate, lock in a value.)
5. Always record temperature information with calibration information in the pH-meter/electrode logbook and on the field sheet.

MEASUREMENT 6.4.4

The pH of sample water is to be measured as soon as possible after removal of the sample from its environmental source. The pH of a water sample can change substantially within hours or even minutes after sample collection as a result of temperature change; degassing (loss of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); in-gassing (gain of sample oxygen, carbon dioxide, hydrogen sulfide, ammonia); mineral precipitation (formation of calcium carbonate, iron hydroxides); metabolic respiration by microorganisms; and other chemical, physical, and biological reactions (Hem, 1989). Field conditions, including rain, wind, cold, dust, direct sunlight, and direct exposure to vehicle exhaust can cause measurement problems.[2] Always protect the instrument system and the measurement process from the effects of harsh weather and transportation damage.

The pH value of an aqueous system should be determined by taking the median of three or more separate and stable measurements that are recorded in a quiescent sample. Recording a median value ensures that the reported pH value represents a true measurement, instead of a computed measurement, and avoids the mathematical procedure required to compute a mean pH from logarithmic operations.

[2]The effects of field conditions on the quality of field measurements, water-quality samples, and data integrity must be anticipated by field personnel and protocols to minimize sample contamination as described in NFM 4 and 5 are to be implemented as standard operating procedure.

TECHNICAL NOTE: The pH value of a given sample always is recorded in the USGS database as a median of a series of stable measurements. For applications that require reporting pH over time (for example, an annual average pH) or space, however, computation of the mean of the hydrogen ion activity may be useful. To compute a series of pH measurements collected over time or space:

a. Take the antilog of each pH measurement, using the following equation: Activity = 10^{-pH}.
b. Add all the antilog values and divide the sum by the total number of values.
c. Convert the calculated mean activity back to pH units, using the equation, pH = (-log10) (mean H^+ activity).

If reporting pH as a computed mean, document this information and the procedure used. **Do not enter a mean pH value in the USGS NWIS database under the parameter code for a median or direct determination of pH.**

6.4.4.A pH MEASUREMENT IN SURFACE WATER

When using a single-parameter pH electrode/meter instrument system, the pH of surface water is determined ex situ, from a quiescent, non-stirred sample that is withdrawn from a churn or cone splitter or other approved sample-compositing device. Although referred to as a single-parameter method, most modern pH meters are equipped with a thermistor used to determine the temperature of the sample. Each pH measurement must be accompanied with a concurrent temperature measurement.

- It is not advisable to immerse the pH electrode into flowing surface water for the following reasons:
  - Placing the pH electrode into moving water risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. In addition, proper functioning of the glass membrane is affected when ionic equilibrium is not achieved with the surrounding sample solution.
  - Calibration of the electrode was accomplished in a quiescent sample, not in flowing or stirred water. Adequate calibration of the instrument system cannot be assumed to extend to moving water.
  - USGS methodology in surface-water measurement usually involves the collection of depth- and width-integrated samples. In situ measurements of pH in a moving water system, either at a singular point in the waterway or across a section, do not meet these requirements.
  - Reference-junction equilibrium cannot be achieved in moving water; thus, correct electrode functioning will again be inhibited.
  - It is difficult to have electrode temperature come to equilibrium with sample temperature in moving water; correct pH instrument system functioning will be inhibited.
- The determination of pH in situ, using a multiparameter instrument system, is described in NFM 6.0 and 6.8. The system selected depends on the data-quality objectives of the study and on site-specific conditions.

Before collecting the sample and making ex situ measurements, it is advisable to determine the range of pH values in the cross section, or estimate the magnitude of lateral mixing of the waterway at the field site, using an in situ measurement method (for example, with a multiparameter sonde).

When making an ex situ pH measurement:

Set up the pH instrument system close to the sampling site in order to minimize the time lapse between sample collection and pH measurement.

1. The glass membrane of the electrode should not contact the sides or bottom of the beaker or other measurement vessel. Use only a clean measurement vessel.
2. Fill the measurement vessel with sufficient sample to ensure that the electrode reference junction is fully immersed, taking care not to aerate the sample.
3. After calibration (or measuring the pH of a different sample), rinse the electrode and thermistor three times with DIW. This crucial step must always be completed between differing solutions.
4. **Rinse the electrode and thermistor sensors two times with the sample**, as follows:
    a. **First rinse—**Pour an aliquot of sample onto the sensors and swirl the sample water around the electrode sensors. Discard the sample appropriately.
    b. **Second rinse—**Pour an aliquot of sample onto the sensors and allow the sensors to sit in the solution for 1 minute (do not swirl). Discard the sample appropriately.
5. **Measure pH**, as follows:
    a. Pour a third aliquot of sample into the vessel. **Allow the sensors to sit in a quiescent sample** for 1 minute or until the pH value stabilizes within the established criterion. Record the pH value on the electronic or paper field-notes form.
    b. Repeat the procedure in (a) above on at least two additional aliquots of the sample, recording the pH measurement for each aliquot on the field form(s).
6. **Calculate a final sample pH as the median** of the values measured for the sample aliquots and document the calculation on field forms.
7. **Record** the final pH value of the sample to the nearest 0.01 pH unit, along with the sample temperature, in paper and (or) electronic field forms, including forms that accompany samples being shipped to the laboratory.
8. The pH value should be reported to the nearest 0.1 pH unit when published and when recorded in the NWIS database.

Always record the temperature of the sample concurrently with each pH measurement.

6.4.4.B pH MEASUREMENT IN GROUND WATER

The pH of ground water should be measured under no-flow (quiescent sample) conditions. When using a single-parameter meter, the measurement can be made either with the pH electrode and temperature sensor inserted (a) into an airtight flowthrough cell or chamber to which the sample is pumped, or (b) in a vessel that contains an aliquot of sample either collected from pump discharge or withdrawn from a sampling device, such as a bailer (figs. 6.4–2 and 6.4–3, respectively). (See NFM 6.8 for pH measurement using a multiparameter sonde).

The central concept for measuring pH in ground water is to use equipment that minimizes aeration, chemical change, and temperature change. If possible, operate equipment in a manner that helps to mitigate losses and gains of dissolved gases in solution.

- The flowthrough cell/chamber method yields accurate pH data when implemented appropriately.
- Bailed or other methods for collecting discrete samples for pH measurement must be implemented carefully to avoid temperature change, turbulence, and sample aeration from decanting and mixing of the bailed water.
- Downhole deployment of a submersible sensor or sonde risks losing the equipment if it becomes lodged in the well.

Document on electronic or paper field forms the methodology used to obtain samples for pH measurement.

Unless specifically required by study objectives or environmental constraints, in situ measurement of pH by putting the sensor system directly into the well (downhole method) should be avoided for the following reasons:

- Placing the pH electrode directly into the borehole risks damage to the delicate glass membrane (scratching, pitting, coating), which will inhibit the correct functioning of the electrode. Any accretions or coatings on the inside of the borehole may be transferred to the pH sensor and damage, or alter, the membrane.
- Pumps, wiring, and (or) other equipment within the borehole may damage or degrade the pH sensor and the sonde.
- Any static electrical charge on the inside of the well casing or borehole may be transferred to the pH electrode, a condition sometimes referred to as a “ground loop,” which also compromises accurate pH measurement.

Always measure and record sample temperature concurrently with pH measurements.

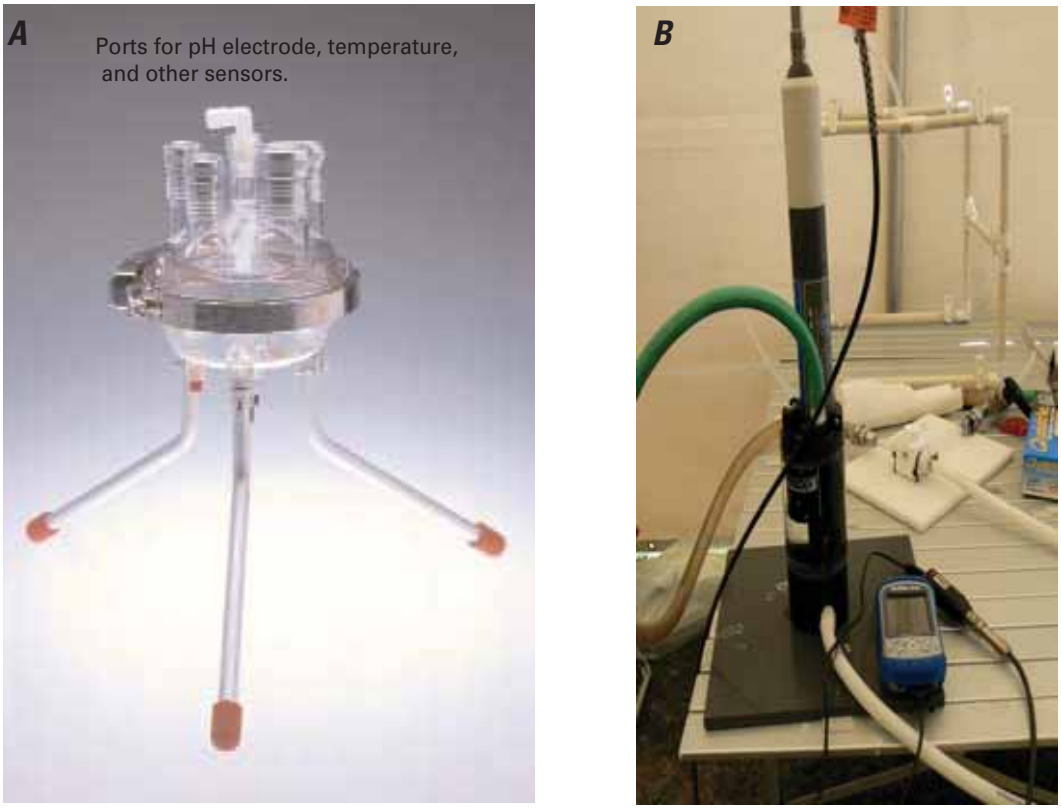


Figure 6.4–2. Photographs of (***A***) a flowthrough cell/chamber for use with single-parameter field-measurement sensors, shown without sensors installed; and (***B***) a flowthrough cell attached to a multiparameter sonde. Photograph ***A*** courtesy of Geotech Environmental. Photograph ***B*** is a USGS stock image.

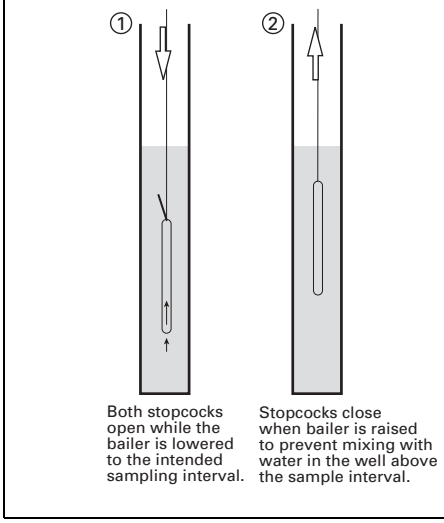


Figure 6.4–3. Use of a dual-valve (double stop-cock) Teflon bailer.

Referring to figure 6.4–2, ground water is pumped directly from the well through tubing and into an airtight flowthrough cell/chamber containing either a calibrated pH electrode and other sensors (typically, dissolved oxygen, specific electrical conductance, and temperature sensors (fig. 6.4–2A), or a multiparameter sonde (fig. 6.4–2B).

After successful calibration of the pH instrument system on site, pH measurement of sample water may proceed either on discrete samples obtained from a bailer, or on pumped ground water circulated through a flowthrough cell/chamber.

- Use of the bailer to obtain ground-water samples is analogous to the approved use of samplers in a surface-water situation, as described below.
- Use of a flowthrough cell/chamber has the advantage of concurrent monitoring of ground-water field measurements in addition to pH, as described below.

To make a pH measurement using a flowthrough cell/chamber system instrumented with single-parameter sensors (fig. 6.4–2):

1. Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight.
2. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged.
3. Check for and eliminate any backpressure condition.
4. Monitor pH variation during purging:
    a. Keep the flow constant and laminar.
    b. Allow the sensors to equilibrate with the ground water for 5 minutes or more, at the flow rate to be used for collecting all of the other samples.
    c. Record pH values at regularly spaced time intervals throughout purging (consult NFM 6.0 for detailed guidance). Compare the variability of pH values toward the end of purging. The stability of pH values is assumed when three to five readings made at regularly spaced intervals are constant. If readings continue to fluctuate, continue to monitor, or, if site conditions are demonstrably variable (degassing, in-gassing, rapid thermal changes from water at depth), select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.
5. Determine sample pH toward the end of purging (for example, during removal of the final purge volume) as follows:
    a. Divert flow from the chamber to allow the sample contained within the chamber to become quiescent (after recording the other field measurements). Record the pH value under quiescent conditions to the nearest 0.01 pH unit.
    b. Determine the median of the pH values recorded under quiescent conditions and report this value as sample pH.
    c. If field personnel have reason to suspect an electrode malfunction, a calibration check at the end of sampling is recommended.

To make a pH measurement on a bailed sample (fig. 6.4–3):

1. Withdraw subsamples from the well and transfer each bailed sample to a churn, cone splitter, or other appropriate compositing device (NFM 2).
2. Remove an aliquot from the sample composite for measurement of pH.

TROUBLESHOOTING 6.4.5

Consult the instrument manufacturer for recommended troubleshooting actions for specific single-parameter and multiparameter pH instrument systems.

- Nearly all problems encountered during pH calibration and measurement can be attributed directly to the condition and responsiveness of the pH electrode (table 6.4–3).
- For any problem, first test that the instrument batteries are fully charged. Keep spare batteries on hand that are fully charged.

Table 6.4–3. Troubleshooting guide for pH measurement.

[DIW, deionized water]

Symptom	Possible cause—Corrective action
Instrument system will not calibrate to full scale	• Buffers may be contaminated or old—Use fresh buffers. • Faulty electrode—Recondition or replace electrode (see section 6.4.2). • Weak batteries—Replace with new or fully charged batteries.
Slow response	***For liquid-filled electrodes:*** • Weak or incorrect solution—Change filling solution to correct molarity. • No or low filling solution—Add fresh solution of correct molarity. • Dirty tip (for example, visible chemical deposits or organic or biological matter on the electrode)—Rinse tip with DIW; if residue persists, use solution and cleaning method recommended by the manufacturer. **Take care not to scratch the electrode tip.** • Clogged or partially clogged junction—Follow the manufacturer's instructions to unclog the junction). • Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B). • Sluggish response to pH changes; pH measurement is biased negatively—Refer to table 6.4–2. ***For gel-filled electrodes:*** • Dirty bulb—Rinse bulb carefully with DIW. If organic/inorganic/biological residue persists, consult the manufacturer's recommendations. • Visibly clogged junction—Follow the manufacturer's instructions to unclog the junction • Water is cold or of low ionic strength—Allow more time for equilibration; consider using a different electrode (section 6.4.3.B).
Erratic readings	• Loose or defective connections—Tighten, clean, or replace connections. • Broken or defective cable—Repair or replace cable. • Static charge—Polish face of meter with antistatic solution. • Loose battery connection—Tighten. • Air bubbles in the electrode bulb—Shake electrode gently. • Too much pressure in flowthrough chamber—Release and reduce pressure. • Weak batteries—Replace with new, fully charged batteries.

6.4.6 REPORTING

Due to the rapidity of pH reactions in environmental samples, the effect of temperature on the operation of the pH instrument system, and chemical and microbiological equilibria within the sample, pH measurements must be completed and recorded as soon as possible after removing the sample from the environmental medium. When entering the pH value for the site into the NWIS database, ensure that the method code selected correctly corresponds to the method that was used for the pH measurement.

- On field forms (electronic or paper) and in the pH-meter/electrode logbook, record pH calibration and environmental measurements to 0.01 standard pH units.
- In the USGS NWIS database, report pH values to the nearest 0.1 standard pH unit, unless study and data-quality objectives dictate otherwise and equipment of the appropriate precision and accuracy has been used.

6.4.7 SELECTED REFERENCES

American Public Health Association, American Water Works Association, and Water Environment Federation, 2001, Standard methods for the examination of water and wastewater (20th ed.): Washington, D.C., American Public Health Association, p. 4–65 to 4–69.

Barnes, Ivan, 1964, Field measurement of alkalinity and pH: U.S. Geological Survey Water-Supply Paper 1535–H, 17 p.

Bates, R.G., 1973, Determination of pH—Theory and practice (2d ed.): New York, John Wiley, 479 p.

Beckman Instruments, Inc., 1986, The Beckman handbook of applied electrochemistry: Fullerton, Calif., Beckman Instruments, Inc., 86 p.

Bellerby, R.G.J., Turner, D.R., Millward, G.E., and Worsfold, P.J., 1995, Shipboard flow injection determination of sea water pH with spectrophotometric detection. Analytica Chimica Acta, v. 309, no. 1, p. 259–270.

Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 129–130.

Busenberg, Eurybiades, and Plummer, L.N., 1987, pH measurement of low-conductivity waters: U.S. Geological Survey Water-Resources Investigations Report 87–4060, 21 p.

Drever, J.I., 1988, The geochemistry of natural waters (2d ed.): Englewood Cliffs, N.J., Prentice-Hall, p. 282–304.

Farquharson, Stuart, Swaim, P.D., Christenson, C.P., McCloud, Mary, and Freiser, Henry, 1992, Fiber optic based pH measurement in a geothermal brine, in Wlodarczyk, M.T., ed., Chemical, Biochemical, and Environmental Fiber Sensors, proceedings: SPIE—The International Society for Optical Engineering, v. 1587, p. 232–239. (Abstract available at http://adsabs.harvard.edu/abs/1992SPIE.1587..232F.)

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 363–364.

Gibs, Jacob, Wilde, F.D., and Heckathorn, H.A., 2007, Use of multiparameter instruments for routine field measurements (ver. 1.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, section 6.8, August, available online only at http://water.usgs.gov/owq/FieldManual/Chapter6/6.8_contents.html. (Accessed October 23, 2008.)

Hem, J.D., 1989, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 61–66.

IC Controls, 2005a, pH theory & measurement: IC Controls Technical Notes Issue 6–1, available online at www.iccontrols.com/files/6-1.pdf. (Accessed September 5, 2008.)

IC Controls, 2005b, Pure water pH measurement in low conductivity samples: IC Controls Applications Notes Issue 6–2, available online at www.iccontrols.com/files/6-2.pdf, (Accessed September 5, 2008.)

Lane, S.L., Flanagan, Sarah, and Wilde, F.D., 2003, Selection of equipment for water sampling (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A2, March, available online only at http://pubs.er.usgs.gov/usgspubs/twri/twri09A2. (Accessed October 23, 2008.)

Nordstrom, D.K., and Alpers, C.N., 1999, Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California: Proceedings of the National Academy of Sciences, v. 96, p. 3455–3462.

Orion Research Inc., 1982, Handbook of electrode technology: Cambridge, Mass., Orion Research Inc., p. P2–P4.

Pankow, J.F., 1991, Aquatic chemistry concepts: Chelsea, Mich., Lewis Publishers, p. 109–127.

pH-meter.info, 2005, pH electrode: pH-meter.info Web page at http://www.ph-meter.info/pH-electrode-construction. (Accessed July 14, 2008.)

Roberson, C.E., Feth, J.H., Seaber, P.R., and Anderson, Peter, 1963, Differences between field and laboratory determinations of pH, alkalinity, and specific conductance of natural water: U.S. Geological Survey Professional Paper 475–C, p. C212–C215.

Raghuraman, B., Gustavson, G., Van Hal, R.E.G., Dressaire, E., and Zhdaneev, O., 2006, Extended-range spectroscopic pH measurement using optimized mixtures of dyes: Applied Spectroscopy, v. 60, no. 12, p. 1461–1468, available online at http://as.osa.org/abstract.cfm?id=121890. (Accessed August 12, 2008.)

Sedjil, M., and Lu, G.N., 1998, A seawater pH determination method using a BDJ detector: Measurement Science and Technology, v. 9, p. 1587–1592, available online at http://www.iop.org/EJ/abstract/0957-0233/9/9/031/. (Accessed August 12, 2008.)

Stumm, Werner, and Morgan, J.J., 1981, Aquatic chemistry—An introduction emphasizing chemical equilibria in natural waters (2d ed.): New York, John Wiley, p. 131–134 and 483–487.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, available online at http://pubs.water.usgs.gov/twri9A.

Wilde, F.D., and Radtke, D.B., 2005, General information and guidelines (ver. 1.2): U. S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, section 6.0, August, available online only at http://water.usgs.gov/owq/FieldManual/Chapter6/6.0_contents.html. (Accessed September 8, 2008,)

Wilde, F.D., ed., 2006, Collection of water samples (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, September, available online only at http://pubs.water.usgs.gov/twri9A4/. (Accessed September 8, 2008.)

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., 2004, Processing of water samples (ver. 2.2): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A5, September, available online only at http://pubs.water.usgs.gov/twri9A5/. (Accessed September 8, 2008.)

Wood, W.W., 1981, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, p. 12.

6.4.8 ACKNOWLEDGMENTS

The authors wish to thank the following USGS scientists for their technical assistance and review of this section of the National Field Manual: D.H. Campbell and J.M. Galloway, who provided peer review, and F.D. Wilde, managing editor of the National Field Manual. Appreciation for editorial and production support is extended to I.M. Collies and L.J. Ulibarri.

SPECIFIC ELECTRICAL CONDUCTANCE 6.3

By D.B. Radtke, J.V. Davis, and F.D. Wilde

Tables

SPECIFIC ELECTRICAL CONDUCTANCE 6.3

By **D.B. Radtke, J.V. Davis, and F.D. Wilde**

Electrical conductance is a measure of the capacity of water (or other media) to conduct an electrical current. Electrical conductance of water is a function of the types and quantities of dissolved substances in water, but there is no universal linear relation between total dissolved substances and conductivity.

The USGS reports conductivity in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C). The method described in this section for measuring conductivity is applicable to surface water and ground water, from fresh to saline.

SPECIFIC ELECTRICAL CONDUCTANCE (CONDUCTIVITY)—a measure of the electrical conductance of a substance normalized to unit length and unit cross section at a specified temperature.

EQUIPMENT AND SUPPLIES 6.3.1

The instrument system used to measure conductivity must be tested before each field trip and cleaned soon after use. Many conductivity instruments are available, including multiparameter instruments that include conductivity sensors. This section provides detailed information on the use of conductivity-specific instruments only, although instructions regarding conductivity standards and measurement methods are applicable in general. Users must be familiar with the instructions provided by the manufacturer. Every conductivity (or multiparameter) instrument must have a log book in which repairs and calibrations are recorded, along with manufacturer make and model description and serial or property number.

.

Table 6.3–1. Equipment and supplies used for measuring conductivity[1]
[°C, degrees Celsius; ≤ , less than or equal to; >, greater than; µS/cm, microsiemens per centimeter at 25 degrees Celsius; L, liter]

- ✓ Conductivity instrument and conductivity sensor
  - Battery powered Wheatstone bridge
  - Direct readout
  - Temperature range at least –5 to +45°C
  - Temperature compensating (25°C)
  - Accuracy: Conductivity ≤100 µS/cm, within 5 percent of full scale
    Conductivity >100 µS/cm, within 3 percent of full scale
- ✓ Thermistor thermometer sensor (for automatic temperature-compensating models)
- ✓ Thermometer, liquid-in-glass or thermistor
- ✓ Extra sensors (if possible) and batteries, or backup instrument
- ✓ Conductivity standards at conductivities that approximate and bracket field values
- ✓ Compositing and splitting device for surface-water samples
- ✓ Flowthrough chamber or downhole instrument for ground-water measurements
- ✓ Plastic beakers (assorted sizes)
- ✓ Soap solution, nonphosphate (1 L)
- ✓ Hydrochloric acid solution, 5 percent volume-to-volume (1 L)
- ✓ Deionized water, 1 L, maximum conductivity of 1 µS/cm
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Brush (small, soft)
- ✓ Waste disposal container
- ✓ Minnow bucket with tether (or equivalent) for equilibrating buffer solutions to sample temperature
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

[1]Modify this list to meet the specific needs of the field effort.

As soon as possible after delivery to the office, label conductivity standards with the date of expiration. Discard standards that have expired, been frozen, have begun to evaporate, or that were decanted from the storage container. Quality-controlled conductivity standards ranging from 50 to 50,000 µS/cm at 25°C can be obtained by USGS personnel through "One Stop Shopping." Order standards outside this range from suppliers of chemical reagents. Conductivity standards usually consist of potassium chloride dissolved in reagent-grade water.

CONDUCTIVITY SENSORS 6.3.1.A

Conductivity sensors are either contacting-type sensors with electrodes or electrodeless-type sensors.

- **Contacting-type sensors with electrodes.** Three types of cells are available: (1) a dip cell that can be suspended in the sample, (2) a cup cell that contains the sample, or (3) a flow cell that is connected to a fluid line. Choose a cell constant on the basis of expected conductivity (table 6.3–2). The greater the cell constant, the greater the conductivity that can be measured. The cell constant is the distance between electrodes (in centimeters) divided by the effective cross-sectional area of the conducting path (in square centimeters).
- **Electrodeless-type sensors.** These operate by inducing an alternating current in a closed loop of solution, and they measure the magnitude of the current. Electrodeless sensors avoid errors caused by electrode polarization or electrode fouling.

Table 6.3–2. Example of cell constants for contacting-type sensors with electrodes and corresponding conductivity ranges

Conductivity range, in microsiemens per centimeter	Cell constant, in 1/centimeter
0.005 – 20	.01
1 – 200	.1
10 – 2,000	1.0
100 – 20,000	10.0
1,000 – 200,000	50.0

CAUTION: Before handling conductivity standards or acids, refer to Material Safety Data Sheets (MSDS) for safety precautions.

6.3.1.B EQUIPMENT MAINTENANCE

Maintenance of conductivity equipment includes periodic office checks of instrument operation. To keep equipment in good operating condition:

- Protect the conductivity system from dust and excessive heat and cold.
- Keep all cable connectors dry and free of dirt.
- Protect connector ends in a clean plastic bag.

Sensor cleaning and storage

Conductivity sensors must be clean to produce accurate results; residues from previous samples can coat surfaces of sensors and cause erroneous readings. Refer to the manufacturer's instructions regarding long- and short-term storage of the sensor.

- Clean sensors thoroughly with deionized water (DIW) before and after making a measurement (this is sufficient cleaning in most cases).
- Remove oily residue or other chemical residues (salts) with a detergent solution. Sensors can soak in detergent solution for many hours without damage.
- If oil or other residues persist, dip the sensor in a dilute hydrochloric acid solution. **Never leave the sensor in contact with acid solution for more than a few minutes.** Check the manufacturer's recommendations before using acid solutions.
- Clean carbon and stainless steel sensors with a soft brush. Never use a brush on platinum-coated sensors.
- Sensors may be temporarily stored in deionized water between measurements and when the system is in daily use.
- For long-term storage, store sensors clean and dry.

CALIBRATION 6.3.2

Conductivity systems must be calibrated before every water-quality field trip and again at each site before samples are measured. Calibration readings are recorded in the instrument log book and on field forms at the time the instrument is calibrated. Remember, the temperature sensor on the conductivity sensor must be District certified within the past 4 months.

Calibration and operating procedures differ, depending on instrument and sensor type.

- Some conductivity sensors may need to be soaked overnight in deionized water before use—Check the manufacturer's instructions.
- Some analog instruments require an initial mechanical zero adjustment of the indicator needle.
- For a cup-type cell, calibration and measurement procedures described for the dip-type cell apply; the only difference is that standards are poured directly into the cup-type cell.
- When using a dip-type cell, do not let the cell rest on the bottom or sides of the measuring container.

Calibrate at your field site— bring standards to sample temperature.

Conductivity systems normally are calibrated with at least two standards. Calibrate sensors against a standard that approximates sample conductivity and use the second standard as a calibration check. The general procedures described in steps 1 through 15 below apply to most instruments used for field measurements—check the instrument manual for specific instructions.

1. Inspect the instrument and the conductivity sensor for damage. Check the battery voltage. Make sure that all cables are clean and connected properly.
2. Turn the instrument on and allow sufficient time for electronic stabilization.

3. Select the correct instrument calibration scale for expected conductivity.
4. Select the sensor type and the cell constant that will most accurately measure expected conductivity.
5. Select two conductivity standards that will bracket the expected sample conductivity. Verify that the date on the standards has not expired.
6. Equilibrate the standards and the conductivity sensor to the temperature of the sample.
   - Put bottles of standards in a minnow bucket, cooler, or large water bath that is being filled with ambient water.
   - Allow 15 to 30 minutes for thermal equilibration. Do not allow water to dilute the standard.
7. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.
   - **First**, rinse the sensor, the thermometer, and the container three times with deionized water.
   - **Next**, rinse the sensor, the thermometer, and the container three times with the standard to be used.
8. Put the sensor and the thermometer into the rinsed container and pour in fresh calibration standard.
9. Measure water temperature. **Accurate conductivity measurements depend on accurate temperature measurements or accurate temperature compensation.**
   - If the sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
   - If using a manual instrument without a temperature display or temperature compensation, adjust the instrument to the temperature of the standard using a calibrated liquid-in-glass or a thermistor thermometer.
10. Agitate a submersible-type conductivity sensor up and down under the solution surface to expel air trapped in the sensor. Read the instrument display. Agitate the sensor up and down under the solution surface again, and read the display. Repeat the procedure until consecutive readings are the same.

11. Record the instrument reading and adjust the instrument to the known standard value.
    - For nontemperature-compensating conductivity instruments, apply a temperature-correction factor to convert the instrument reading to conductivity at 25°C.
    - The correction factor depends to some degree on the specific instrument used—use the temperature-correction factor recommended by the manufacturer. If this is not available, use correction factors from table 6.3–3.
    - If an instrument cannot be adjusted to a known calibration standard value, develop a calibration curve. After temperature compensation, if the percentage difference from the standard exceeds 5 percent, refer to the troubleshooting guide (section 6.3.4).
12. Record in the instrument log book and on field forms:
    - The temperature of the standard solution.
    - The known and the measured conductivity of the standard solution (including ± variation).
    - The temperature-correction factor (if necessary).
13. Discard the used standard into a waste container. Thoroughly rinse the sensor, thermometer, and container with deionized water.
14. Repeat steps 7 through 13 with the second conductivity standard.
    - The purpose for measuring a second standard is to check instrument calibration over the range of the two standards.
    - The difference from the standard value should not exceed 5 percent.
    - If the difference is greater than 5 percent, repeat the entire calibration procedure. If the second reading still does not come within 5 percent of standard value, refer to the troubleshooting guide in section 6.3.4 or calibrate a backup instrument.
15. Record in the instrument log book and on field forms the calibration data for the second standard.

Do not use expired standards.
Never reuse standards.

Table 6.3–3. Correction factors for converting non-temperature-compensated values to conductivity at 25 degrees Celsius, based on 1,000 microsiemens potassium chloride solution

[Use of potassium-based constants on non-potassium-based waters generally does not introduce significant errors for general purpose instruments used to measure conductivity]

Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor
0.5	1.87	10.5	1.39	20.5	1.09
1.0	1.84	11.0	1.37	21.0	1.08
1.5	1.81	11.5	1.35	21.5	1.07
2.0	1.78	12.0	1.33	22.0	1.06
2.5	1.76	12.5	1.32	22.5	1.05
3.0	1.73	13.0	1.30	23.0	1.04
3.5	1.70	13.5	1.28	23.5	1.03
4.0	1.68	14.0	1.27	24.0	1.02
4.5	1.66	14.5	1.26	24.5	1.01
5.0	1.63	15.0	1.24	25.0	1.00
5.5	1.60	15.5	1.22	25.5	0.99
6.0	1.58	16.0	1.21	26.0	0.98
6.5	1.56	16.5	1.19	26.5	0.97
7.0	1.54	17.0	1.18	27.0	0.96
7.5	1.52	17.5	1.16	27.5	0.95
8.0	1.49	18.0	1.15	28.0	0.94
8.5	1.47	18.5	1.14	28.5	0.93
9.0	1.45	19.0	1.13	29.0	0.92
9.5	1.43	19.5	1.12	29.5	0.91
10.0	1.41	20.0	1.11	30.0	0.90

To extend the temperature range shown in table 6.3–3, consult the manufacturer's guidelines. If these are unavailable, use the following equation:

$$C_{25} = \frac{C_m}{1 + 0.02(t_m - 25)}$$

where,
C_{25}= corrected conductivity value adjusted to 25°C;
C_m = actual conductivity measured before correction; and
t_m = water temperature at time of C_m measurement.

MEASUREMENT 6.3.3

In situ measurement generally is preferred for determining the conductivity of surface water; downhole or flowthrough-chamber measurements are preferred for ground water. Be alert to the following problems if conductivity is measured in an isolated (discrete) sample or subsample:

- The conductivity of water can change over time as a result of chemical and physical processes such as precipitation, adsorption, ion exchange, oxidation, and reduction—Do not delay making conductivity measurements.
- Field conditions (rain, wind, cold, dust, direct sunlight) can cause measurement problems—Shield the instrument to the extent possible and perform measurements in a collection chamber in an enclosed vehicle or an on-site laboratory.
- For waters susceptible to significant gain and loss of dissolved gases, make the measurement within a gas-impermeable container (Berzelius flask) fitted with a stopper—Place the sensor through the stopper and work quickly to maintain the sample at ambient surface-water or ground-water temperature.
- Avoid contamination from the pH electrode filling solution—Measure conductivity on a separate discrete sample from the one used for measuring pH; in a flowthrough chamber, position the conductivity sensor upstream of the pH electrode.

Conductivity must be measured at the field site.

Document the precision of your measurements. Precision should be determined about every tenth sample or more frequently, depending on study objectives. Successive measurements should be repeated until they agree within 5 percent at conductivity ≤ 100 µS/cm or within 3 percent at conductivity > 100 µS/cm.

The conductivity measurement reported must account for sample temperature. If using an instrument that does not automatically temperature compensate to 25°C, record the uncompensated measurement in your field notes, along with the corrected conductivity value. Use correction factors supplied by the instrument manufacturer if available; otherwise, refer to table 6.3–3.

6.3.3.A SURFACE WATER

Surface-water conductivity should be measured in situ, if possible; otherwise, determine conductivity in discrete samples collected from a sample splitter or compositing device. Filtered samples may be needed if the concentrations of suspended material interfere with obtaining a stable measurement.

In situ measurement

Conductivity measurements in flowing surface water should represent the cross-sectional mean or median conductivity at the time of observation (see step 7, below). Any deviation from this convention must be documented in the data base and with the published data.

First:

- Take a cross-sectional conductivity profile to determine the degree of system variability. A submersible sensor works best for this purpose.
- Refer to NFM 6.0 for criteria to help decide which sampling method to use.

Next, follow the 7 steps listed below:

1. Calibrate the conductivity instrument system at the field site after equilibrating the buffers with stream temperature.
2. Record the conductivity variation from a cross-sectional profile on a field form and select the sampling method.
   - **Flowing, shallow stream—**wade to the location(s) where conductivity is to be measured.
   - **Stream too deep or swift to wade—**lower a weighted conductivity sensor from a bridge, cableway, or boat. Do not attach weight to the sensor or the sensor cable.
   - **Still-water conditions—**measure conductivity at multiple depths at several points in the cross section.
3. Immerse the conductivity and temperature sensors in the water to the correct depth and hold there (no less than 60 seconds) until the sensors equilibrate to water conditions.
4. Record the conductivity and corresponding temperature readings without removing the sensors from the water.
   - Values should stabilize quickly to within 5 percent at conductivity ≤100 µS/cm and within 3 percent at conductivity >100 µS/cm.
   - Record the median of the stabilized values on field forms.
   - If the readings do not meet the stability criterion after extending the measurement period, record this difficulty in the field notes along with the fluctuation range and the median value of the last five or more readings.
5. For EWI or EDI measurements, proceed to the next station in the cross section and repeat steps 3 and 4. Record on field forms the mean (or median, if appropriate) value for each subsection measured.
6. When the measurement is complete, remove the sensor from the water, rinse it with deionized water, and store it.
7. Record the stream conductivity on the field forms:
   - **In still water—median** of three or more sequential values.
   - **EDI—mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
   - **EWI—mean or median** of all subsections measured (see NFM 6.0).

Subsample measurement

Representative samples are to be collected and split or composited according to approved USGS methods (NFM 4). Measure the conductivity of samples as soon as possible after collection. If the sample cannot be analyzed immediately, fill a bottle to the top, close it tightly, and maintain the sample at stream temperature until measurement.

Reported conductivity values normally are determined on an unfiltered sample. Large concentrations of suspended sediment can be a source of measurement error—record such conditions in the field notes.

- If sediment concentrations are heavy, measure conductivity on both unfiltered and filtered subsamples and record both values on the field form.
- If the conductivity value differs significantly between the filtered and unfiltered samples, report the filtered value as sample conductivity and identify it as a "filtered sample."

1. Calibrate the conductivity instrument system at the field site.
2. Select the sampling method (see NFM 6.0) and collect a representative sample.
3. Withdraw a homogenized subsample from a sample splitter or compositing device. Rinse the sample bottles three times with the sample—rinse them with sample filtrate, for filtered samples.
4. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.
    a. First, rinse the sensor, the thermometer, and the container three times with deionized water.
    b. Next, rinse the sensor, the thermometer, and the container using sample water.
5. Allow the sensors to equilibrate to sample temperature, then discard the used sample water. Pour fresh sample water into a container holding the sensor and the thermometer. **When using a dip-type sensor, do not let the sensor touch the bottom or sides of the measuring container.**

6. Measure water temperature.
   - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
   - If the instrument is not temperature compensating, use a calibrated thermistor or a liquid-in-glass thermometer.
   - Adjust the instrument to the sample temperature (if necessary) and remove the thermometer.
7. Measure conductivity.
   a. Remove any air trapped in the sensor by agitating the sensor up and down under the water surface.
   b. Read the instrument display.
   c. Agitate the sensor up and down under the water surface, and read the display again.
   d. Repeat the procedure until consecutive readings are the same.
8. Record the conductivity and the sample temperature on field forms.
   - If the instrument is not temperature compensating, record the raw data and convert the values to conductivity at 25°C using temperature-correction factors provided by the manufacturer.
   - Report the median of the readings to three significant figures on the field forms.
   - Discard the sample into a waste container and dispose according to regulations.
9. **Quality control—**
   - Repeat steps 3 through 8 with at least two fresh subsamples, rinsing the instruments once only with sample water.
   - Subsample values should be within ±5 percent for conductivity ≤100 µS/cm, or ±3 percent for conductivity >100 µS/cm.
   - If criteria cannot be met: filter the samples, report the median of 3 or more samples, and record this difficulty in field notes.
10. Rinse the sensor, the thermometer, and the container with deionized water. If another measurement is to be made within the next day or two, store the sensor in deionized water. Otherwise, store the sensor dry.

6.3.3.B GROUND WATER

Measurements of ground-water conductivity must represent aquifer conditions. Temperature changes resulting from transporting a well sample to land surface can affect conductivity.

- To minimize the effect from temperature changes, measure conductivity as close to the source as possible, using either a downhole or flowthrough-chamber sampling system (refer to NFM 6.0 for details).
- Bailed or other methods for collecting discrete samples isolated from the source are not recommended as standard practice, although such methods are sometimes called for owing to site characteristics or other study requirements.
- The well should be purged or in the process of purging before sample conductivity is determined and recorded.

Downhole and flowthrough-chamber measurement

1. Calibrate the conductivity instrument system on site.
   - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
     a. Check the temperature of the water flowing into the bucket against that of standards.
     b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
   - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.
2. Install the conductivity and temperature sensors.
   - **Downhole system—**Lower the conductivity and temperature sensors to the sampling point, followed by the pump.

a. Remove any air from the system by agitating the conductivity sensor up and down under the water; read the instrument display.
b. Repeat this procedure until rapid consecutive readings are approximately the same.

- **Flowthrough-chamber system—**Install the chamber system as close to the well as possible and shield the system from direct sunlight.

a. Position the conductivity sensor upstream from the pH electrode.
b. Direct flow to the chamber after an initial discharge to waste to clear sediment from sample line.
c. Release any air trapped in the chamber.
d. Agitate the conductivity sensor up and down under the water to remove air from system. Rapid consecutive readings should be about the same.

3. During purging (table 6.0–1 in NFM 6.0):
   - Keep flow constant and laminar.
   - Allow the sensors to equilibrate with ground-water temperature for 5 minutes or more at the flow rate to be used for collecting all other samples.
4. Measure conductivity and associated temperature at regular intervals throughout purging; record the conductivity values and the associated temperature in the field notes.
   - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
   - If the instrument is not temperature compensating, install a calibrated thermometer in the flowthrough chamber, record raw data, and apply correction factors.
5. Check the variability of the conductivity values toward the end of purging.
   - The stability criterion is met when five readings taken at regularly spaced intervals of 3 to 5 minutes or more are within
     ±5 percent for conductivity ≤100 µS/cm
     ±3 percent for conductivity >100 µS/cm

- When readings fluctuate rapidly, record the median of three or more readings within about 60 seconds as the value for a specific time interval.
- If the criterion is not met, extend the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals. Record this difficulty on the field forms.

6. Report conductivity.
   - Record the final five values on field forms.
   - Report the median value of the final five measurements as the sample conductivity.
   - If values exceed the stability criterion, report the range of values observed for the time interval, along with the median of the final five or more values.

Subsample measurement

Conductivity measurements reported from bailed or other discrete samples need to be identified in the data base, indicating the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

1. Calibrate the conductivity instrument system onsite.
   - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
     a. Check the temperature of the water flowing into the bucket against that of standards.
     b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
   - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.

2. Draw off subsamples for measurement.
    - **Quality control—Collect three subsamples to check precision.**
    - If samples need to be stored for a short time, or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles—fill to the brim, cap tightly, and maintain at ambient ground-water temperature. Measure conductivity as soon as possible.
3. Follow procedures described in steps 4 through 10 for "Subsample measurement" of surface water (6.3.3.A).

> **TECHNICAL NOTE:** If the sample is measured in an open container and readings do not stabilize within several minutes, the cause may be CO_2 degassing—use a closed system to measure the sample. Filter the conductivity sample if the settling of clay particles appears to interfere with the stability of the readings.

TROUBLESHOOTING 6.3.4

Contact the instrument manufacturer if the actions suggested in table 6.3–4 fail to resolve the problem.

- If available, use a commercial, electronic calibrator to check the function of conductivity instruments.
- Check the voltage of batteries. Always have good batteries in instruments and carry spares.

Table 6.3–4. Troubleshooting guide for conductivity measurement
[HCl, hydrochloric acid; ºC, degrees Celsius]

Symptom	Possible cause and corrective action
Will not calibrate to standards	• Standards may be old or contaminated—use fresh standards. • Electrodes dirty—clean with a detergent solution, then with 5 percent HCl. Before using any acid solution to remove resistant residues, check manufacturer's guidelines. • Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. • Weak batteries—replace. • Temperature compensation incorrect—ensure that thermometer is operating properly and is calibrated. • Sensor constant incorrect—replace sensor.
Erratic instrument readings	• Loose or defective connections—tighten or replace. • Broken cables—repair or replace. • Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. • Rapid changes in water temperature—measure in situ. • Outgassing of ground-water sample—use a downhole instrument; if unavailable, use a flowthrough chamber. • Broken sensor—replace.
Instrument requires frequent recalibration	• Temperature compensator not working—measure conductivity of a solution. Place solution in a water bath and raise solution temperature to about 20ºC. Measure conductivity again, allowing sufficient time for temperature of conductivity sensor to equilibrate to temperature of solution. If the two values differ by 5 percent or more, replace conductivity sensor.

REPORTING 6.3.5

Report routine conductivity measurements to three significant figures, whole numbers only, in microsiemens per centimeter at 25°C.

- Record the accuracy range of the instrument system in the data base, if possible, and always report it with published values.
- Enter field-determined conductivity measurements on the NWQL Analytical Services Request form using the correct parameter code.

SELECTED REFERENCES

American Public Health Association, American Water Works Association, and Water Environment Federation, 2001, Standard methods for the examination of water and wastewater (20th ed.): Washington, D.C., American Public Health Association, p. 2–43 to 2–48.

American Society for Testing and Materials, 1977, Standard test methods for electrical conductivity and resistivity of water, No. D 1125–77: Philadelphia, American Society for Testing and Materials, p. 138–146.

Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 148–150.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 461–463.

Hem, J.D., 1982, Conductance—a collective measure of dissolved ions, *in* Minear, R.A., and Keith, L.H., eds., Water analysis, v. 1, inorganic species, pt. 1: New York, Academic Press, p. 137–161.

_____ 1985, Study and interpretation of chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 66–69.

Rainwater, F.H., and Thatcher, L.L., 1960, Methods for collection and analysis of water samples: U.S. Geological Survey Water-Supply Paper 1454, p. 275–278.

Roberson, C.E., Feth, J.H., Seaber, P.R., and Anderson, Peter, 1963, Differences between field and laboratory determinations of pH, alkalinity, and specific conductance of natural water: U.S. Geological Survey Professional Paper 475– C, p. C212–C215.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, available online at http://pubs.water.usgs.gov/twri9A.

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., September 1999, Collection of water samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed Sept. 20, 2005 at http://pubs.water.usgs.gov/twri9A4/

Wood, W.W., 1981, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, p. 11.

DISSOLVED OXYGEN 6.2

Revised by **Michael E. Lewis**

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

DISSOLVED OXYGEN 6.2

The concentration of dissolved oxygen in water is affected by many factors including ambient temperature, atmospheric pressure, and ion activity. Accurate data on the concentration of dissolved oxygen (DO) in environmental water resources are essential for documenting changes that result from natural phenomena and human activities. Sources of DO in water include atmospheric aeration and photosynthetic activities of aquatic plants. Many chemical and biological reactions in ground water and surface water depend directly or indirectly on the amount of available oxygen. Dissolved oxygen is necessary in aquatic systems for the survival and growth of many aquatic organisms and is used as an indicator of the health of surface-water bodies.

DISSOLVED OXYGEN:
molecular oxygen
(oxygen gas)
dissolved in water.

Standard field methods used by the U.S. Geological Survey (USGS) for determining concentrations of DO in surface and ground waters include the use of amperometric and luminescent-based-sensor instruments and spectrophotometric analysis. Selection of a measurement method should take into consideration environmental conditions, the specific data-quality objectives of the data-collection program, and the inherent benefits of a given technology. Except where noted, these methods are used routinely to determine the concentration of dissolved oxygen in fresh to saline unfiltered surface and ground waters.

- The amperometric method (section 6.2.1) has been the standard USGS procedure for the past 10 to 15 years for determining aquatic DO concentrations that exceed 1 milligram per liter (mg/L).
- The luminescent-based sensor method (section 6.2.1) uses relatively new technology, and applies to the same environmental conditions as the amperometric method.
- The spectrophotometric method (section 6.2.2 - for example, the Rhodazine-D™[1] technique) is recommended for determining concentrations of DO less than 2.0 mg/L.
- The iodometric (Winkler) method (section 6.2.3) is regarded as an accurate and precise method for the determination of dissolved oxygen in water; however, it is not a standard USGS method for field determinations of DO because the accuracy and reproducibility achieved depend largely on knowledge of the presence of possible sources of interference (nitrite, ferrous or ferric iron, and organic matter, for example) and on the experience and technique of the data collector. In a laboratory environment, the method is excellent for calibrating DO instrument systems.

Some procedures for equipment operation recommended in this guidance document may not apply to your equipment as a result of recent technological advances. Document any changes made to standard USGS procedures.

[1]Rhodazine-D™, a colorless reduced dye, is a proprietary product of CHEMetrics, Incorporated, and constitutes less than 1 volume percent of solution in the ampoule. Additional constituents in the ampoule are water, diethylene glycol, tris(hydroxymethyl)aminomethane, and potassium hydroxide.

AMPEROMETRIC AND LUMINESCENT-SENSOR METHODS 6.2.1

The amperometric and luminescent-sensor methods are appropriate for routine measurement of DO concentrations under most of the field conditions encountered by USGS data-collection personnel. Calibration procedures are similar for these methods.

- **The amperometric method** has been the most commonly used field method for measuring DO in water for USGS data-collection efforts. The DO concentration is determined using a temperature-compensating meter connected to a polarographic-membrane type of sensor.
  - The method is relatively simple to use and is well-suited to making discrete or continuous in situ measurements of DO concentration in surface water or ground water.
  - Method performance can be negatively affected by calibration drift; by loose, wrinkled, or damaged membranes; or by sensor contact with hydrogen sulfide. Unfortunately, poor performance can occur without any indications from the instrument readings.
- **The luminescent-sensor** technology that has been developed for environmental monitoring of DO in water is considered an appropriate alternative to the amperometric method. The luminescent-sensor method involves the measurement of light-emission characteristics of a luminescent-based reaction at the sensor-water interface (see **TECHNICAL NOTE**). While the relative benefits of the technology are apparent, it should be recognized that its application at typical USGS sampling sites is relatively new; therefore, it does not benefit from the experience derived from years of use, as is the case with the amperometric method.
  - There are no consumables such as membranes or filling solutions with the new method, unlike the amperometric method.
  - The technology does not consume oxygen at the sensor-water interface; therefore, no stirring is required in slow or stagnant water.
  - There are no known sources of interference to the method in natural aquatic systems.

TECHNICAL NOTE: The luminescent sensor employs a light-emitting diode (LED) to provide incident light, which excites the oxygen-sensitive luminescent-dye molecule substrate (luminophore) of the sensor. After dissipation of the excitation energy, longer-wavelength light is emitted (luminescence). The magnitude of steady-state luminescence (intensity)—that is, the average luminescent lifetime (the phase difference between the excitation light and the returned light)—is measured by the sensor and is inversely proportional to the DO concentration in the water.

6.2.1.A EQUIPMENT AND SUPPLIES

DO instruments (meters and sensors) are available from a number of commercial vendors. Because the instructions for use, calibration, and maintenance often differ for each manufacturer, the user is cautioned to read and carefully follow the instructional manual for the instrument system to be used. DO instruments, and expecially the sensors, are sophisticated electronic equipment and require care in handling and operation. The equipment and supplies required for the amperometric and luminescent-sensor methods of measuring the DO concentration in a water body are listed in table 6.2-1.

- Amperometric instrument systems consist of the entire sensor assembly, including the electrolyte solutions, membranes, and thermistor thermometers.
- Protect sensors and other supplies from being jostled during transportation, from sudden impacts, sudden temperature changes, and extremes of heat and cold.
- Follow the manufacturer's recommendations for short-term (field) and long-term (office) storage of sensors and for performance checks.

Table 6.2–1. Equipment and supplies for the amperometric and luminescent-sensor methods of dissolved-oxygen determination[1]

[DO, dissolved oxygen; mg/L, milligrams per liter; NFM, *National Field Manual for the Collection of Water-Quality Data*; –, minus; +, plus; °C, degrees Celsius; and ±, plus or minus]

- ✓ Amperometric instrument must be temperature and pressure compensated
- ✓ Amperometric instrument: DO sensor membrane replacement kit includes membranes, O-rings, filling solution

For amperometric or luminescent-sensor methods:

- ✓ DO instrument and DO sensor or multiparameter instrument with DO capability and digital temperature readout display
  Operating range at least -5°C to +45°C
  Measure concentrations 0.05 to 20 mg/L
  Minimum scale readability, preferably 0.01 mg/L DO
  Calibrated accuracy within ±0.2 mg/L DO
- ✓ Calibration chamber, per manufacturer's recommendation
- ✓ Pocket altimeter-barometer, calibrated; measures to nearest 1 millimeter
- ✓ Thermometer (see NFM 6.1 for selection and calibration criteria)
- ✓ Zero DO calibration solution[2]; dissolve 1 gram sodium sulfite and a few crystals of cobalt chloride in 1 liter deionized water
- ✓ Flowthrough chamber for determining DO in ground water
- ✓ Oxygen solubility table (table 6.2-6)
- ✓ Waste disposal container or equivalent
- ✓ Spare batteries
- ✓ Calibration and maintenance log books for DO instrument and barometer

[1]Modify this list to meet specific needs of the field effort.
[2]Prepare fresh zero DO solution before each field trip.

Before each field trip:

1. Check the instrument batteries and all electrical connections.
2. **When using an amperometric instrument,** inspect the sensor closely, checking for any loose, wrinkled, or torn membrane, air bubbles beneath the membrane, and a tarnished or discolored cathode or anode. If any of these problems are detected, do not use the sensor until it has been serviced according to the manufacturer's recommendations.
3. Test instrument calibration. Do not use an instrument that fails to calibrate properly. Service the instrument according to the manufacturer's recommendations and recalibrate.
4. Test the instrument to ensure that it will read zero in a freshly prepared zero DO solution. For amperometric instruments:
   - If the instrument reading exceeds 0.2 mg/L, then the sensor membrane and electrolyte (if present) need to be replaced or the sensor needs to be repaired.
   - Before repairing or replacing the sensor, check zero DO again with a freshly prepared zero DO solution.
5. Check the calibration with a pocket altimeter-barometer. If necessary, recalibrate following the manufacturer's recommendations.

CAUTION:
Before handling any chemicals, refer to the Material Safety Data Sheet (MSDs) for safety precautions.

The relation between sensor membranes and temperature must be recognized. DO sensors must be temperature compensating: the permeability of the membrane and solubility of oxygen in water change as a function of temperature.

- All built-in thermistor thermometers must be calibrated and field checked before use, as described in NFM 6.1 ("Temperature").
- Some manufacturers provide membranes of different thicknesses, the selection of which is based on the intended use of the instrument. Select the sensor membrane based on manufacturer recommendations.
- Two basic types of membrane design are available: (a) loose membranes and (b) membrane cap assemblies. Loose membranes are considerably less expensive but are more difficult to install. Sensor performance can be affected by the manner in which loose membranes are installed and conditioned after installation.
- After membrane replacement, allow a minimum of 2 to 6 hours for the new membrane to condition before calibration and use.
  - For greater stability during calibration allow the new membrane to condition overnight prior to calibration.
  - If conditions necessitate using the sensor and new membrane before the recommended overnight conditioning time, more frequent calibration checks and possibly recalibration are necessary for accurate DO measurements.

Luminescent-based sensors: Manufacturers of luminescent-based DO sensors can provide very different guidance on the care and maintenance of their particular sensor. Read and follow the manufacturer's guidance for the specific instrument to be used.

6.2.1.B CALIBRATION

Instrument systems for the amperometric or the luminescent-sensor methods must be properly calibrated and tested before each field trip and cleaned in the field after each use.

- **Amperometric instruments**

  Different manufacturers recommend different calibration frequencies for membrane-electrode DO meters; however, virtually all state that optimum instrument performance and data quality will be obtained by frequent calibration. Calibration and operation procedures for the amperometric method differ among instrument types and makes—refer to the manufacturer's instructions.

- **Luminescent-sensor instruments**

  Luminescent-based sensors are precalibrated by the manufacturer and most manufacturers' literature suggests that no further calibration is warranted. The accuracy of factory calibrations, however, may not satisfy the data-quality objectives of a specific program. **Frequency of calibration can have a significant effect on the overall accuracy and precision of DO measurements; therefore, users of these meters are advised to make frequent calibration checks and to recalibrate as frequently as required to meet specific data-quality objectives.**

One-point and two-point calibrations

Calibration for most amperometric DO instruments and some luminescent-sensor instruments can only be checked with a 1-point calibration at 100-percent saturation. For these instruments, a zero DO check should be performed routinely as an evaluation of sensor performance (see section 6.2.1.A, "Before each field trip"). Because the sensors on DO instruments may be slow to respond after the zero check, the sensor should be thoroughly rinsed with deionized water before use.

Some instruments allow for 2-point calibrations at 0-percent and 100-percent saturation. Follow the manufacturer's instructions for those instruments with 2-point calibration functionality. **Verifying instrument performance at zero DO and using a 2-point calibration can be particularly important for data accuracy when the instrument will be used to measure low DO concentrations (less than 5 mg/L).**

Correction for atmospheric pressure and salinity

Atmospheric pressure, the temperature of the water or water vapor, and the conductivity (or salinity) of the water must be known to determine the theoretical amount of oxygen that can be dissolved in water. **Record all calibration information in instrument log books and copy calibration data onto field forms at the time of calibration.**

Ambient atmospheric pressure is true atmospheric pressure at the measurement site, not that which has been adjusted to sea level. Atmospheric pressure reported by the National Weather Service generally is not the true (ambient) value. Weather Service atmospheric readings usually are adjusted to sea level and must be adjusted back to the elevation of the weather station. Upon request, a weather station may provide ambient atmospheric pressure.

- Use a calibration-checked pocket altimeter-barometer to determine ambient atmospheric pressure to the nearest 1 millimeter (mm) of mercury.
- Check the accuracy of all field barometers before each field trip, and record readings and adjustments in the log book. If possible, check barometer accuracy with information from an official weather station.
- Use table 6.2–2 and figure 6.2–1 if the value used for atmospheric pressure has been adjusted to sea level.
- To correct weather station readings adjusted to sea level to ambient atmospheric pressure: subtract appropriate values shown (table 6.2–2, fig. 6.2–1) from atmospheric readings adjusted to sea level (shown in millimeters of mercury).

Although atmospheric pressure does not decrease linearly with increases in elevation, linear interpolation is acceptable within the elevation ranges given in table 6.2–2. Alternatively, plot the values from table 6.2–2 and extrapolate subtraction factors directly from the graph (fig. 6.2-1). Section 6.2.5 contains the table of oxygen solubility at various temperatures and pressures. Many instruments have the pressure-temperature algorithm stored in internal memory. Interactive tables also are available for user-specified temperature, pressure, and salinity at http://water.usgs.gov/software/dotables.html (accessed Apr. 27, 2006).

Check DO meter calibration at each field site. In addition, amperometric instruments should be recalibrated each time after a meter has been powered off.

Table 6.2–2. Factors used to correct atmospheric pressures adjusted to sea level

[NGVD, National Geodetic Vertical Datum of 1929]

Elevation of weather station (in feet, NGVD)	Value to subtract (millimeters of mercury)
0	0
1,000	27
2,000	53
3,000	79
4,000	104
5,000	128
6,000	151

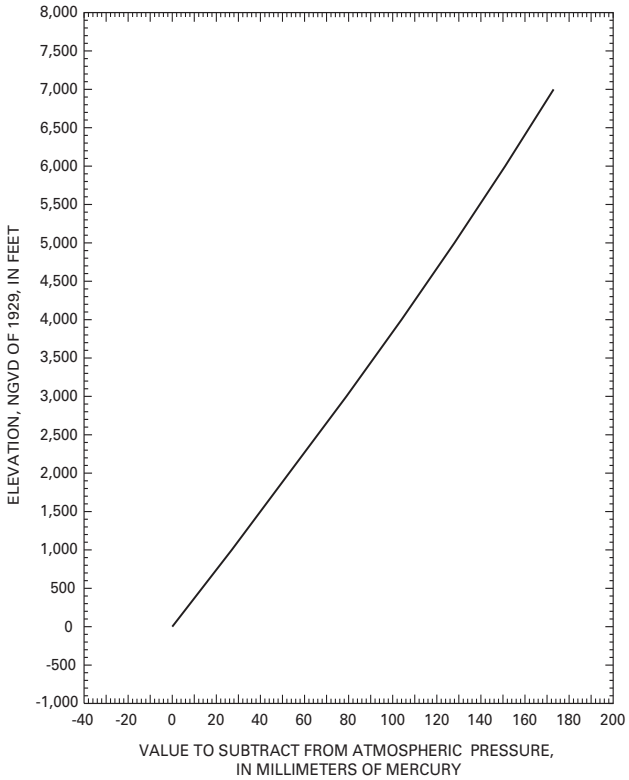


Figure 6.2–1. Factors used to correct atmospheric pressures adjusted to sea level

Although the salinity correction can be made either during calibration or after measurement, **the preferred USGS method is to apply salinity correction factors after calibration and measurement** (recalibration is necessary for each field variation in salinity if the correction is made during calibration). For salinity-correction procedures, see section 6.2.5.

Calibration procedures

The three procedures described below are for a one-point calibration (100-percent saturation) of a DO system. The iodometric method for DO measurement described in section 6.2.3 can be used to check the calibration of these instruments. Record all calibration information in instrument log books and copy calibration data onto field forms at the time of calibration.

- **Procedure 1 (Air-calibration chamber in air) and Procedure 2 (Calibration with air-saturated water)** can be used with minor modifications for either amperometric or luminescent-sensor instruments.
- **Procedure 3 (Air-calibration chamber in water)** is appropriate only for the amperometric method.
- Many amperometric DO sensors require the meter to be turned on for 10 to 15 minutes before calibration and use to stabilize the probe. Refer to the manufacturer's instrument-specific guidelines for the requirements of your instrument.

Procedure 1—Air-calibration chamber in air

This procedure is similar to Procedure 3 (Air-calibration chamber in water), which commonly is used for amperometric instruments, except that the calibration chamber is in air rather than in water. This calibration method is most commonly recommended by manufacturers of amperometric instruments. Calibration chambers are either built into the instrument case or are provided as separate components by the manufacturer. **Use the calibration chamber provided or recommended by the manufacturer.**

1. Wet the inside of the calibration chamber with water. Then pour out the water (but leave a few drops). Remove any water droplets on the sensor membrane and insert the sensor into the chamber (this ensures 100-percent humidity).
2. If using an amperometric instrument, allow 10 to 15 minutes for the DO sensor and the air inside the calibration chamber to equilibrate.

3. Using your calibration pocket altimeter-barometer, read the ambient atmospheric pressure checked to the nearest 1 mm of mercury.
4. Measure the temperature in the calibration chamber and observe the readings until the instrument stabilizes. Read the temperature to the nearest 0.1°C. The temperature inside the chamber should approximate the water temperature, measured with a calibrated thermometer.

TECHNICAL NOTE FOR AMPEROMETRIC INSTRUMENTS: Most instrument manufacturers recommend calibrating at temperatures that are at least within 10°C of the ambient water temperature. The most accurate calibration will be achieved if the temperature difference between the environmental water and the calibration chamber is minimized as much as possible.

5. Use the oxygen-solubility table 6.2–6 to determine the DO saturation at the measured temperature and atmospheric pressure. (Refer to section 6.2.5 and table 6.2–7 for salinity corrections.)
6. Following the manufacturer's instructions, adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table.

   Verify that the instrument reading is within ± 0.2 mg/L of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality requirements of the study. **The luminescent-sensor instrument is now calibrated and ready for use.**

7. When working with an amperometric instrument, remove the sensor from the calibration chamber and check to see if any water droplets are on the membrane. **Water droplets on the membrane cause improper calibration. If water droplets are present, recalibrate the instrument; otherwise the instrument is now calibrated and ready for use.**

Procedure 2—Calibration with air-saturated water

In this procedure, the DO sensor or instrument system is calibrated against water that is saturated with oxygen at a known temperature and ambient atmospheric pressure.

1. The temperature of water used for calibration should be about the same as the temperature and conductivity of the water to be measured.
   - **If working at the field site—**obtain about 1 liter (L) of water from the water body to be measured.
   - **If working in the laboratory—**obtain about 1 L of deionized water or tap water.
2. Place the DO sensor and calibration water in a large beaker or open-mouth container. (Some manufacturers supply an air-saturated water-calibration vessel.)
   - Allow the sensor to come to thermal equilibrium with the water temperature.
   - Shield the beaker or container from direct sunlight and wind to minimize temperature variations.
3. Aerate the water for 5 to 10 minutes. Using a battery-operated aquarium pump or minnow-bucket aerator and a short piece of tubing, attach a gas diffusion stone to the end of the tubing and place it at the bottom of the beaker of calibration water. Avoid placing the instrument in the stream of air bubbles.
4. Determine if the water is 100-percent saturated with oxygen.
   - Observe the instrument reading while aerating the calibration water.
   - When no change in the DO reading is observed on the instrument for 4 to 5 minutes, assume that the water is saturated.
5. Using your pocket altimeter-barometer, read the ambient atmospheric pressure to the nearest 1 mm of mercury.
6. Read the temperature of the calibration water to the nearest 0.1°C.
7. Using oxygen solubility table 6.2–6, determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.5 and table 6.2–7 for salinity corrections.)

   ➔ **Skip to Step 9 if using an amperometric instrument**

8. **For luminescent-sensor instruments:** Following the manufacturer's instrument calibration instructions, verify that the instrument reading is within ± 0.2 mg/L of the computed saturation value. (Alternatively, apply a more stringent accuracy criterion that reflects study data-quality requirements.) **The luminescent-sensor instrument is now calibrated and ready for use.**

9. **For amperometric instruments:** Adequate flow of water across the surface of the membrane is required for accurate measurements. Recommendations for flow velocity vary by manufacturer, with most recommending about 1 foot per second (ft/s).

   - Provide suitable turbulence in the air-saturated water by physical or mechanical means to maintain the required flow rate past the membrane, avoiding the creation of air bubbles at the water-sensor interface.
   - Maintain this flow rate when making measurements and adjusting instrument calibration.

10. **For amperometric instruments**: Turn off the aerator and take care to prevent any air bubbles from adhering to the membrane. Following the manufacturer's instructions, set or adjust the calibration control until the instrument reads a saturation value of DO as determined above. Verify that the instrument reading is within ± 0.2 mg/L of the computed saturation value, or use more stringent accuracy criteria that reflect the data-quality objectives of the study.

For accurate calibration, be sure that the water is 100 percent saturated with oxygen (step 4 above).

Procedure 3—Air-calibration chamber in water

This calibration method is applicable only to amperometric instruments. An air-calibration chamber permits calibration of the DO sensor at the temperature of the water in which the DO concentration is to be measured. This calibration procedure minimizes errors caused by temperature differences. Air-calibration chambers for in-water calibrations currently are not available on the open market and one of the most common, the YSI 5075A calibration chamber, is no longer manufactured. For most multi-parameter water-quality instruments, the manufacturer-provided ground-water flow cell may be modified and used as an air-calibration chamber in water. The modification requires the cell to be mounted on the sonde with one port of the cell plugged and the other port vented to the atmosphere with tubing.

1. Insert the sensor probe into the rings of the DO wand and dip this calibration chamber into the surface or ground water to be measured, allowing the temperature readings to stabilize. Remove the wand and pour out the excess water, leaving a few drops.
   - Check for and remove any water droplets on the sensor membrane.
   - Insert the DO sensor into the wet chamber (this ensures 100 percent humidity).
   - If a YSI model 5739 sensor is used, the pressure-compensating diaphragm on the side of the sensor must be enclosed within the calibration chamber during calibration.
   - Check that no water can leak into the calibration chamber and that the membrane does not have droplets of water adhering to it. The water droplets reduce the rate of oxygen diffusion through a membrane, producing erroneous results.
2. Immerse the calibration chamber into the water to be measured. Allow 10 to 15 minutes for the air temperature inside the chamber to equilibrate with the water (see the **TECHNICAL NOTE** in Procedure 1).
   - For streams, choose an area of the stream that closely approximates mean stream temperature. In shallow streams, try to place the chamber in an area that represents the stream but that is shaded from direct sunlight.
   - For ground water, use temperature-stabilized purge water or other clean water having a temperature that closely approximates that of the ground water.

Water droplets on the DO membrane will result in improper calibration. Recalibration is required if water droplets are observed.

3. Using a calibration-checked pocket altimeter-barometer, determine the ambient atmospheric pressure to the nearest 1 mm of mercury.
4. Read the temperature within the chamber to the nearest 0.1°C, using a calibrated thermometer (NFM 6.1).
   - The temperature inside the chamber should approximate the water temperature.
   - If the two temperatures do not match, allow additional time for equilibration of the chamber with the water temperature.
   - If the temperature of the chamber still does not approximate the water temperature, the thermistor in the DO sensor might be malfunctioning. Compare water temperature measured by the DO meter and a calibrated field thermometer. If the two measurements vary by more than ± 0.2°C, the calibration should be discontinued and the DO meter thermistor should be repaired following the manufacturer's recommendations.

   TECHNICAL NOTE: Most instrument manufacturers recommend calibrating at temperatures that are at least within 10°C of the ambient water temperature. The most accurate calibration will be achieved if the temperature difference between the environmental water and the calibration chamber is minimized as much as possible.

5. Use table 6.2-6 (section 6.2.5) to determine the DO saturation value at the measured water temperature and atmospheric pressure. If a salinity correction will be applied during calibration, consult the instructions in section 6.2.5 and table 6.2-7.
6. Following the manufacturer's instructions, set or adjust the calibration control until the instrument reads a DO saturation value determined from oxygen solubility (table 6.2–6). Verify that the instrument reading is within ± 0.2 mg/L of the computed saturation value, or use more stringent accuracy criteria per the data-quality objectives of the study. The instrument is now calibrated and ready for use. Remove the sensor from the calibration chamber.

TECHNICAL NOTE: The YSI 5075A calibration chamber is designed to allow the membrane surface of a DO electrode (model 5739) to be at ambient atmospheric pressure while in the chamber. Because the pressure-compensating diaphragm must remain at atmospheric pressure, check the calibration chamber vent tube (from the chamber through the end of the handle) to ensure that it is not plugged with debris or filled with water.

MEASUREMENT 6.2.1.C

The solubility of oxygen in water depends on the partial pressure of oxygen in air, the temperature of the water, and the dissolved-solids content of the water.

- The higher the atmospheric pressure and the lower the temperature and conductivity, the more oxygen can be dissolved in the water.
- Degassing, mineral precipitation, and other chemical, physical, and biological reactions can cause the DO concentration of a water sample to change substantially within minutes after sample collection. These sample reactions are especially important when sampling ground water that is not in equilibrium with the atmosphere.

The solubility of oxygen in water decreases as salinity increases. **Correction factors for salinity normally are applied after measuring DO.** Information about oxygen solubility and salinity and a salinity correction-factors table are in section 6.2.5. Interactive tables also are available according to user-specified temperature, pressure, and salinity at http://water.usgs.gov/software/dotables.html (accessed Apr. 27, 2006).

Surface water

Standard determinations of dissolved oxygen in surface water represent the cross-sectional median or mean concentration of dissolved oxygen at the time of observation.

- Measuring the DO concentration at one distinct spot in a cross section is valid only for flowing water with a cross-sectional DO variation of less than 0.5 mg/L. Discerning such variation requires a cursory cross-section measurement. The effort involved in collecting this cross-section information is only slightly less than making an equal-width-increment (EWI), equal-discharge-increment (EDI), or multiple-vertical cross-sectional measurement. Measurements made at multiple locations in the cross section are recommended when possible.

- Determining DO for a single vertical at the centroid of flow at the midpoint of the vertical only represents the cross section under ideal mixing conditions.
- Do not measure DO in or directly below sections with turbulent flow, in still water, or from the bank, unless these conditions represent most of the reach or are required by the study objectives.
- Apply a salinity correction to the saturation values after the DO measurement, if needed (http://water.usgs.gov/software/dotables.html, accessed Aug. 26, 2005).

Dissolved oxygen must be measured in situ. Never measure DO in subsamples from a sample splitter.

Follow the 7 steps below to measure DO in surface water:

1. Calibrate the DO instrument at the field site and check that the temperature thermistor has been certified by the USGS Water Science Center within the past 4 months (NFM 6.1.2).
2. Record the DO variation from the cross-sectional profile and select the sampling method (NFM 6.0):

   - **Flowing, shallow stream**—Wade to the location(s) where DO is to be measured.
   - **Stream too deep or swift to wade**—Lower a weighted DO sensor with a calibrated temperature sensor from a bridge, cableway, or boat. (Do not attach the weight directly to the sensors or sensor cables, because this could damage the sensors or sensor cables.)
   - **Still-water conditions**—Measure DO at multiple depths at several points in the cross section.

3. Immerse the DO and temperature sensors directly into the water body and allow the sensors to equilibrate to the water temperature (no less than 60 seconds).

   Notes for amperometric instruments only:

   - If the water velocity at the point of measurement is less than about 1 ft/s, use a stirring device or stir by hand to increase the velocity. (To hand stir, raise and lower the sensor at a rate of about 1 ft/s, but do not break the surface of the water.) The stir-by-hand method may not be appropriate in lakes, reservoirs, or slow-moving waters (for example, bayous) as these water bodies may be stratified at the point of measurement, making accurate DO measurements impossible. This could be especially problematic in areas where DO concentrations change substantially over short distances, such as near the thermocline or bottom sediments.
   - High stream velocity can cause erroneous DO measurements.

4. Record the temperature without removing the sensor from the water.
5. After the instrument reading has stabilized, record the median DO concentration (see NFM 6.0).
   - The reading should stabilize to within ±0.2 mg/L.
6. For EWI, EDI, or multiple-vertical measurements, proceed to the next station in the cross section and repeat steps 3 through 5. When measurements for the stream have been completed, remove the sensor from the water, rinse it with deionized water, and store it according to the manufacturer's instructions.

7. Record DO concentrations on the field forms:
   - **In still water**—median of three or more sequential values.
   - **EDI**—mean value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
   - **EWI—mean (or median)** of all subsections measured.

Ground water

To determine the concentration of DO in an aquifer, the water being measured must not contact air. Study objectives and site characteristics will dictate the specific procedures selected. **If the DO concentration is less than 1 mg/L, refer to the spectrophotometric method (section 6.2.2).**

- Throughout measurement, use equipment that avoids aeration, and operate equipment to mitigate losses or gains of dissolved gases. (Consult NFM 6.0 for proper downhole and flowthrough-chamber sampling procedures.)
- Use a positive-displacement submersible pump and high-density plastic or fluorocarbon-polymer sample tubing that is relatively gas impermeable, if possible.
- Use transparent materials for the tubing and chamber to allow checking for bubbles. Air bubbles that adhere to the sides of the tubing and flowthrough chamber will add significant error to low-level DO measurements (A.F. White, U.S. Geological Survey, written commun., 1993).

Never use a bailed or other discrete sampler to determine the concentration of DO in ground water.

Follow the steps below to measure DO in ground water:

1. Calibrate the DO instrument onsite. Check that the thermistor thermometer has been certified by the USGS Water Science Center within the past 4 months.
2. Install the DO equipment (see NFM 6.0):
   - **Downhole system**—Lower the DO and temperature sensors to the sampling point, followed by the pump, to monitor DO variation during purging. If an amperometric downhole system will be used only for final DO determination after the samples are collected and the pump is removed, attach a stirrer to the DO instrument before lowering it to the sampling point.
   - **Flowthrough-chamber system**—Refer to NFM 6.0 for installation guidelines. Be sure to:

a. Install the DO sensor through an air-tight grommet, checking that the seal is intact. Check that the sensors are properly immersed.
b. Flush air bubbles from the tubing walls and flowthrough chamber—tap the tubing with the blunt end of a tool to dislodge entrained air bubbles (see TECHNICAL NOTE below).
c. Check for and eliminate backpressure in the chamber.

3. If using a luminescent-sensor instrument, skip to step 4. If using an amperometric instrument, be sure to maintain constant, laminar flow past the DO sensor.
4. Measure and record DO at regular intervals throughout purging. Allow the sensors to equilibrate with ground water for 5 minutes or more at the flow rate to be used for sampling.
5. Check the stability (variability) of DO toward the end of purging.

   The stability criterion is met when five consecutive readings made at regularly spaced intervals of 3 to 5 minutes or more are within ±0.2 mg/L. (For each reading, monitor fluctuations for 30 to 60 seconds and record the median value, if necessary.) If the ±0.2 mg/L criterion is not met, increase the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals.
6. Report sample DO as the median of the final five DO readings recorded. Record on field forms any difficulty with stabilization.
7. Remove the sensor from the water and rinse it with deionized water.

TECHNICAL NOTE: Anomalously high DO measurements commonly are caused by aeration of ground water during pumping. This can result from air leakage through loose fittings on production-well pumps (for example, turbine pumps) and also if drawdown in the aquifer introduces air into the cone of depression or through well-screen perforations. To avoid these problems, review information about the pump, well-construction and drawdown data, and previous data records (A.F. White, U.S. Geological Survey, written commun., 1993).

Air bubbles in the lines and flowthrough chamber can add substantial error to low DO readings.

6.2.1.D TROUBLESHOOTING (AMPEROMETRIC INSTRUMENTS)

The troubleshooting suggestions given in table 6.2–3 are for amperometric instruments and are not exhaustive; consult the manufacturer of your amperometric instrument for additional guidance. Consult the manufacturer to address problems with a luminescent-sensor instrument. Faulty batteries can cause erratic readings.

- Check the voltage of the batteries.
- Start with good batteries in the instrument and carry spares.

Table 6.2–3. Troubleshooting guide for amperometric instruments

Symptom	Possible cause and corrective action
Instrument drifts or takes excessive time to stabilize	• Thermal equilibrium of water and sensor has not been reached—wait longer. • Weak batteries—replace. • DO sensor needs maintenance—recondition.
Erratic instrument readings	• Break in cable—replace cable. • Faulty connection at instrument or sensor—clean contact and tighten. • Hole in membrane—replace membrane, recondition. • Air bubble in sensor—recondition sensor. • Weak batteries—replace.
Instrument too slow to react	• Gold cathode tarnished—buff with pencil eraser and recondition sensor. • Fouled membrane— replace membrane and recondition sensor.
Instrument will not read zero in sodium sulfite solution	• Solution contains oxygen—make fresh solution. • Instrument still does not read zero—replace membrane and recondition sensor.
Instrument cannot be calibrated to read standards	• Unable to adjust upward—check to see in more than one membrane is on the sensor. • Unable to adjust downward (membrane probably too tight or too thin)—replace membrane.
Instrument reads inaccurate temperature	• Faulty thermistor—repair or replace.

SPECTROPHOTOMETRIC METHOD 6.2.2

Spectrophotometric methods[2] described by Chemetrics, Inc. are recommended for accurate determination of DO concentrations in suboxic waters over a concentration range of 0.1 mg/L to approximately 1.0 mg/L. The Rhodazine-D™ colorimetric method minimizes atmospheric interaction with the water sampled (ASTM D 5543-94, 2005; White and others, 1990; http://www.chemetrics.com/catalogpdfs.html, accessed May 15, 2006).

- The accuracy of the method is ±10 percent at 75 percent of full range, ±20 percent at 25 percent of full range, and ±30 percent at the CHEMetrics practical detection limit.
- The technique was developed for ground water but it can be adapted for work in anoxic zones of lakes and reservoirs.

EQUIPMENT AND SUPPLIES 6.2.2.A

Two sampling systems can be used, an in situ (submersible or downhole) sampler (see White and others, 1990), or a plastic overflow cell through which sample water is pumped. Either sampling system uses partially evacuated oxygen-free glass ampoules containing Rhodazine-D™ that are broken along a prescored capillary tip while they are submerged in the water to be analyzed. Equipment and supplies needed for this method are listed in table 6.2–4.

[2]Dissolved-oxygen concentrations in the range of 0.2 to 2.0 mg/L and 2.0 to 15.0 mg/L also can be determined spectrophotometrically using an Indigo-Carmine method (Gilbert and others, 1982; www.chemetrics.com/catalogpdfs.html, accessed May 15, 2006)

Table 6.2–4. Equipment and supplies for the spectrophotometric method of dissolved-oxygen determination

[mm, millimeter; DO, dissolved-oxygen concentration; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

- ✓ Portable spectrophotometer, capable of accepting a 13-mm-diameter ampoule, or CHEMetrics multianalyte photometer (catalog no. V-2000 or V-1000)
- ✓ Vacu-vial® kit CHEMetrics, Inc., Catalog number K-7553™ for a DO range of 0.1 to 0.8 mg/L when using a spectrophotometer or the V-1000 photometer, and 0.1 to 1.4 mg/L. when using the V-2000 photometer. (Note! The V-1000 is being discontinued.).
- ✓ Submersible sampling tool, used in situ, to meet criteria described in White and others (1990). For example,
  - Downhole sampler, or
  - Plastic sampler tube (overflow cell) and short length of C-flex tubing
- ✓ Safety gloves, glasses, and apron
- ✓ Waste disposal container
- ✓ White background sheet
- ✓ Deionized water (maximum conductivity of 1 µS/cm)
- ✓ Bottle, squeeze dispenser, for deionized water

Photometers and visual kits are described by CHEMetrics, Inc., for a variety of concentration ranges. White and others (1990) used a portable Milton Roy Minispect-10™ battery-powered spectrophotometer. Any spectrophotometer of equal or better quality can be used if it can accept a 13-mm-diameter cell and is adjustable to a wavelength of 555 nanometers.

6.2.2.B CALIBRATION AND INTERFERENCES

Dissolved oxygen is measured as percent absorbance by the spectrophotometer.

- A calibration chart is provided in each CHEMetrics kit, along with a regression formula to convert absorbance to micrograms per liter of DO for use with the spectrophotometer. No other standards are provided. CHEMetrics photometers are pre-calibrated for direct readout.
- The CHEMetrics kit contains a blank ampoule used to zero a spectrophotometer or the CHEMetrics V-2000 photometer. The CHEMetrics V-1000 photometer is supplied with a "VVR Zeroing ampoule.
- Interferences from total salinity, major dissolved inorganic species, dissolved gases, or temperature are negligible.

- The spectrophotometric method is affected by the presence of reducible inorganic species such as chlorine, ferric and cupric ions, and hexavalent chromium, resulting in high-biased DO readings. The presence of cupric copper and ferric iron at less than 50 micrograms per liter (µg/L) cause a bias of less than 1 µg/L; at concentrations of 100 µg/L, cupric copper causes a bias of 5 µg/L and ferric iron causes a bias of 7µg/L. The effect from reducible inorganic species can be corrected if the concentrations of the interfering species are known (White and others, 1990).
- Additional calibration is needed if the method will be used to determine DO in heavily contaminated or acidic waters. This can be done by equilibrating a water sample with known partial pressures of atmospheric oxygen (White and others, 1990). Atmospheric oxygen standards are available from suppliers of gas chromatography equipment.
- Color and turbidity interfere with this test method, causing positively biased results. If using this method in colored or turbid water, first conduct an assessment of the amount of bias attributable to such effects.

MEASUREMENT 6.2.2.C

Rhodazine-D™ reagent reacts with DO to produce an oxidized complex characterized by a red-blue color. The color intensity is proportional to the concentration of the initial DO present.

Follow the 8 steps below to measure DO using the spectrophotometric method:

1. According to site characteristics and study objectives, purge the well following guidelines in NFM 4.2.
2. Set the spectrophotometer to a wavelength of 555 nanometers.
3. Zero the spectrophotometer using the blank provided in the kit (follow the manufacturer's instructions). Collect the sample.
4. Install either the downhole sampling tool (White and others, 1990) or use a plastic overflow-sampler tube with a suitable pump. (Use a positive-displacement submersible pump and high-density plastic or fluorocarbon polymer sample tubing that is relatively gas impermeable, if possible, throughout measurement; use equipment that avoids aeration; and operate equipment to mitigate losses or gains of dissolved gases—consult NFM 6.0 for proper downhole and flowthrough-chamber sampling procedures.)

- **Downhole system—**

  a. Carefully lower a sampling tool attached to a wire line.

  b. At the collection point (in a well or in surface water), break the scored tip of the ampoule using a sharp upward tug on the sampling tool. (This permits sample water to be drawn into the ampoule. During transit to the surface, progressively decreasing pressure in the ampoule prevents cross contamination from overlying water through the capillary tip.)

  c. Withdraw the ampoule from the sampler and mix the contents of the ampoule by inverting it several times, allowing the bubble to travel from end to end.

  d. Wipe all liquid from the exterior of the ampoule, using a lint-free tissue.

- **Overflow cell—**

  a. Purge the well (NFM 4.2).

  b. Connect the plastic overflow-sampler tube provided by CHEMetrics, Inc., to the outlet of the ground-water pump tubing with a short length (2 inches or less) of C-flex tubing. Reduce the pump flow rate to about 500 milliliters (mL) per minute for sample collection. Continue pumping the well and allow the sample tube to overflow during sample collection.

     - Use optically clear materials for the tubing and chamber (to check that entrained bubbles are not present). Air bubbles that adhere to the sides of the tubing and flowthrough chamber will add significant error to low-level DO measurements (A.F. White, U.S. Geological Survey, written commun., 1993).

     - Flush air bubbles from the tubing walls and flowthrough chamber. Tap the tubing with the blunt end of a tool to dislodge entrained air bubbles.

  c. Insert the glass ampoule, tip first, into the overflowing sampler tube so that the tapered tip is at the bottom of the tube.

  d. Snap the tip by gently pressing the upper end of the ampoule toward the wall of the sampling tube.

  e. The ampoule will fill, leaving a bubble to facilitate mixing. Mix the contents of the ampoule by inverting it several times, allowing the bubble to travel from end to end.

  f. Wipe all liquid from the exterior of the ampoule, using a lint-free tissue.

5. Insert the ampoule directly into the 13-mm-diameter spectrophotometer cell holder immediately after retrieval.
6. Read absorbance:
   - Make spectrophometer readings as soon as possible after snapping the tip of the ampoule, optimally within 30 seconds.
   - Read each DO value three times and record the median value.
7. Calculate the DO concentrations using regression equations provided by CHEMetrics, Inc. (White and others, 1990).
8. **Quality control—**
   - Repeat steps 5 through 7 twice to document precision.
   - To document the variability of DO concentrations within the water system, repeat steps 3 through 7 on three sequentially collected samples.

IODOMETRIC (WINKLER) METHOD 6.2.3

The USGS currently uses the Alsterberg-Azide modification to the Winkler titration procedure for iodometric determination of dissolved oxygen. **The accuracy of measurements using the iodometric method should be within at least ±0.05 mg/L.**

- The iodometric method currently is not being used as a standard field method in USGS investigations for measurement of dissolved oxygen because (1) the accuracy achievable can be variable and is dependent on the experience and technique of the data collector, (2) potential environmental interferences require advanced knowledge of sample chemistry, and (3) field conditions can make preventing exposure of the sample to atmospheric oxygen difficult. Nevertheless, use of the iodometric method can produce accurate results when correctly implemented.
- The iodometric (Winkler) method is excellent for calibrating DO instrument systems in a laboratory environment.
  - — When calibrating amperometric instruments in the laboratory using the Winkler procedure, deionized water saturated with air is titrated to determine the DO; the DO instrument is then adjusted to the concentration determined from the titration.
  - — If a saline solution is used to approximate the environmental water, do not apply a salinity correction factor.

6.2.3.A EQUIPMENT AND SUPPLIES

Equipment and supplies needed for the iodometric method are listed in table 6.2–5. The procedure involves the use of reagent packets available in premeasured pillow packets from commercial suppliers, or prepared as described in Skougstad and others (1979) and American Public Health Association (2005). Clean all equipment before use.

Table 6.2–5. Equipment and supplies for the iodometric (Winkler) method of dissolved-oxygen determination

[mL, milliliter; *N*, normal; µS/cm, microsiemens per centimeter at 25 degrees Celsius; NFM, *National Field Manual for the Collection of Water-Quality Data*]

- ✓ Beaker, 2,000 mL, glass or Teflon™
- ✓ Bottles for biological oxygen demand (BOD) analysis, glass stoppered, 300 mL
- ✓ Stirrer, magnetic
- ✓ Stirring bars, Teflon™ coated
- ✓ Cylinder, graduated, 250 mL
- ✓ Flask, Erlenmeyer, 250 mL
- ✓ Buret, 25-mL capacity with 0.05-mL graduations and Teflon™ stopcock
- ✓ Buret, support stand
- ✓ Buret, clamp, double
- ✓ Alkaline iodide-azide reagent
- ✓ Manganous sulfate reagent
- ✓ Sulfamic acid granules
- ✓ Sodium thiosulfate, 0.025 *N* titrant
- ✓ Starch indicator solution
- ✓ Clippers, for opening reagent pillows
- ✓ Appropriate safety gloves, glasses, and apron
- ✓ Waste disposal container
- ✓ White background sheet
- ✓ Deionized water (maximum conductivity of 1 µS/cm)
- ✓ Bottle, squeeze dispenser, for deionized water
- ✓ Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
- ✓ Pocket altimeter-barometer, calibrated, Thommen model 2000™ or equivalent

MEASUREMENT 6.2.3.B

Measure DO on at least two subsamples, for quality control. Results of two iodometric titrations should agree within 0.1 mg/L. If they do not agree, repeat the titration on a third subsample.

Follow steps 5 and 6 to perform the iodometric titration in duplicate. If the purpose is to check calibration of an amperometric or luminescent-sensor instrument, start at step 1 and continue to the end.

1. Fill a 2,000-mL beaker with deionized water that is near DO saturation. The water temperature should be close to the ambient (field or laboratory) temperature.
2. Prepare the DO instrument for operation according to the manufacturer's instructions.
3. Place the DO sensor in a beaker of distilled water. With a magnetic stirrer, maintain a velocity of at least 1 ft/s past the DO sensor.
4. Monitor the DO concentrations of the deionized water with the DO instrument and record the value after the readings have stabilized.
5. Carefully fill two biochemical oxygen demand (BOD) bottles with deionized water from the beaker, taking care to avoid introducing any air bubbles, and overflowing the bottles adequately to remove any trapped air bubbles.
6. Determine the DO concentration of the water in each BOD bottle, as follows:
   a. Add one each of the following dry reagent pillow packets:
      - alkaline iodide-azide (white powder).
      - manganous sulfate (pinkish-colored powder).
   b. Recap the bottle. **Do not allow air bubbles to be trapped in the bottle.**
   c. Invert the bottle 25 times or more to completely dissolve the reagents.
      - An orange-brown flocculent indicates the presence of DO.
      - Allow the flocculent to settle halfway down the bottle (approximately 5 minutes).
      - Invert the bottle 25 times again; let the flocculent settle again until the upper half of the solution is clear.
   d. Add one reagent pillow of sulfamic acid.

e. Recap the bottle without introducing air or air bubbles. Invert the bottle 25 times until all of the flocculent and granules are dissolved, leaving a yellow color.

f. Fill a clean 25-mL buret with 0.025 *N (Normal)* sodium thiosulfate titrant. Remove any air bubbles from the delivery tube beneath the stopcock and zero the meniscus.

g. Use a clean, graduated cylinder to measure 200 mL of the sample and pour the sample into a clean, wide-mouth Erlenmeyer flask.

h. Place the flask on a magnetic stirrer. Add a clean Teflon™ stirring bar and stir the sample at a moderate rate **without aerating the sample.**

i. Add increments of sodium thiosulfate titrant until the color turns pale straw-yellow.

j. Add 1 to 2 mL of starch indicator solution. (This causes the sample to turn dark blue.)

k. Very slowly add more sodium thiosulfate titrant until the sample just turns clear. (A white background behind the bottle will help you see the color change.)

l. Record the volume of sodium thiosulfate titrant used, in milliliters.

- For a 200-mL sample, the volume of titrant added is directly proportional to the amount of DO in milligrams per liter.
- To calculate DO for a sample volume greater or less than 200 mL,

$$DO\ (mg/L) = \left(\frac{200}{sample\ volume}\right) \times titrant\ added,\ in\ mL$$

m. Record the DO value. Rinse the equipment with deionized water.

n. **Quality control**—The titration values for the duplicate samples should agree within 0.1 mg/L. If they do not, repeat the titration on a third sample.

7. Recheck the field instrument for proper functioning, following the manufacturer's instructions. Adjust the calibration control until the DO instrument system reads the DO concentration determined from the iodometric measurement.

REPORTING 6.2.4

USGS personnel are instructed to enter the DO value on the National Water Quality Laboratory Analytical Services Request form and on the field form.

- DO concentrations are determined to the nearest 0.1 mg/L.
- If the concentration exceeds 20 mg/L, report ">20 mg/L."
- Note that the percentage of DO saturation in water can be greater than 100.

CORRECTION FACTORS FOR OXYGEN SOLUBILITY AND SALINITY 6.2.5

Correction factors for the solubility of oxygen at various temperatures and pressures and for salinity based on conductivity are given in tables 6.2–6 and 6.2–7, respectively. Tables 6.2–6 and 6.2–7 were generated from the equations of Weiss (1970) and can be customized to cover the range and decimal places needed (see U.S. Geological Survey Quality of Water Branch Technical Memorandum 81.11, 1981). Interactive software to generate a specific range of oxygen-solubility and salinity correction factors can be accessed at http://water.usgs.gov/software/dotables.html (accessed Apr. 28, 2006).

To convert oxygen-saturation values for salinity, use correction factors based on chloride concentration or conductivity. Refer to the manufacturer's instructions for the DO instrument before applying a salinity correction.

- Correcting DO solubility for saline waters (salinities greater than 2,000 microsiemens per centimeter or 1,000 mg/L chloride) varies with instrument type, calibration method, and the salts in solution.
- The correction based on conductivity (table 6.2–7) is more useful because accurate conductivity can be determined easily from a field measurement. Salinity correction factors based on chloride can be calculated using information provided in U.S. Geological Survey Quality of Water Branch Technical Memorandum 79.10, 1979.

- DO instruments use either an automatic internal salinity correction, a manual salinity control knob for internal correction, or the calibration control knob for manual salinity correction.
- Check that instruments with automatic internal salinity correction use approved salinity correction factors.

Example of salinity correction:

$$8.2\ mg/L \times 0.951 = 7.8\ mg/L$$

where,

8.2 mg/L is 100-percent DO saturation from table 6.2–6,
0.951 is the correction factor from table 6.2–7, and
7.8 mg/L is the corrected value.

For this example, you would adjust the DO instrument to 7.8 mg/L from 8.2 mg/L.

To express results as percent saturation, use the following equation:

$$DO\ (percent\ saturation) = \frac{measured\ DO\ (mg/L)}{DO\ (mg/L\ at\ 100\ percent\ saturation)} \times 100$$

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures

[From R.F. Weiss (1970). Temp °C, temperature in degrees Celsius; atmospheric pressures from 695 to 600 millimeters mercury begin after 40°C]

Temp	Atmospheric pressure, in millimeters of mercury																			
°C	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	700
0.0	15.3	15.2	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4
0.5	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2
1.0	14.8	14.7	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	13.1
1.5	14.6	14.5	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	13.1	13.0	12.9
2.0	14.4	14.3	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7
2.5	14.2	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.5
3.0	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.5	12.4
3.5	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	12.2
4.0	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	12.2	12.1	12.0
4.5	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.1	12.0	11.9
5.0	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7
5.5	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.7	11.6
6.0	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4
6.5	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.9	11.8	11.7	11.6	11.5	11.5	11.4	11.3
7.0	12.7	12.6	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	11.1
7.5	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0
8.0	12.4	12.3	12.2	12.1	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9
8.5	12.2	12.1	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7
9.0	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.8	10.7	10.6
9.5	11.9	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	10.5
10.0	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4
10.5	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2
11.0	11.5	11.4	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.3	10.2	10.1
11.5	11.4	11.3	11.2	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0
12.0	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	9.9
12.5	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8
13.0	11.0	10.9	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7
13.5	10.9	10.8	10.7	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.6
14.0	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5
14.5	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	700
15.0	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3
15.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.2
16.0	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9.1
16.5	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.4	9.3	9.2	9.2	9.1	9.0	9.0
17.0	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9
17.5	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8
18.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.7
18.5	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6
19.0	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5
19.5	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4
20.0	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3
20.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3
21.0	9.3	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2
21.5	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1
22.0	9.1	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0
22.5	9.0	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9
23.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9
23.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8
24.0	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7
24.5	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6
25.0	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6
25.5	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5
26.0	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4
26.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4
27.0	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3
27.5	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2
28.0	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2
28.5	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1
29.0	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0
29.5	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp	Atmospheric pressure, in millimeters of mercury																			
°C	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	700
30.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9
30.5	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9
31.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8
31.5	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7
32.0	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7
32.5	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6
33.0	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6
33.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5
34.0	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6	6.6	6.5	6.5
34.5	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4
35.0	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3
35.5	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
36.0	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
36.5	7.1	7.0	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2
37.0	7.0	7.0	6.9	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1
37.5	7.0	6.9	6.9	6.8	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1
38.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0
38.5	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0
39.0	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	6.0
39.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	6.0	5.9
40.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.9

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp	Atmospheric pressure, in millimeters of mercury																			
°C	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
0.0	13.3	13.2	13.1	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5
0.5	13.1	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3
1.0	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2
1.5	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.0
2.0	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9
2.5	12.4	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.0	10.9	10.8	10.7
3.0	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6
3.5	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5	10.4
4.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3
4.5	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.3	10.3	10.2
5.0	11.6	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1	10.0
5.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9
6.0	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	9.9	9.9	9.8
6.5	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7	9.7
7.0	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.3	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6	9.5
7.5	10.9	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4
8.0	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6	9.5	9.5	9.4	9.3
8.5	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.3	9.3	9.2
9.0	10.5	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1
9.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.0	9.0
10.0	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	8.9	8.9
10.5	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8	8.8
11.0	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7	8.7
11.5	9.9	9.9	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6	8.6
12.0	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7	8.7	8.6	8.5	8.5
12.5	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.6	8.6	8.5	8.4	8.4
13.0	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.5	8.5	8.4	8.3	8.3
13.5	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.2	8.2
14.0	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1
14.5	9.3	9.2	9.2	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
15.0	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9
15.5	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8
16.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.7
16.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7
17.0	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.6	7.6
17.5	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5
18.0	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.5	7.5	7.4
18.5	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.3
19.0	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3
19.5	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.2	7.2
20.0	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1
20.5	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0
21.0	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0
21.5	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9
22.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.8
22.5	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8
23.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7
23.5	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6
24.0	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6
24.5	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5
25.0	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.4
25.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.4	6.4
26.0	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4	6.4	6.3
26.5	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
27.0	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
27.5	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2
28.0	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.1	6.1
28.5	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1	6.1	6.0
29.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1	6.1	6.0	6.0
29.5	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp	Atmospheric pressure, in millimeters of mercury																			
°C	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
30.0	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9
30.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8
31.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8
31.5	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7
32.0	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7
32.5	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6
33.0	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6
33.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5
34.0	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5
34.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4
35.0	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4
35.5	6.2	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3
36.0	6.2	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3
36.5	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.2
37.0	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2
37.5	6.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2
38.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2	5.1
38.5	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1
39.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0
39.5	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0
40.0	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0	5.0

Table 6.2–7. Salinity correction factors for dissolved oxygen in water (based on conductivity)

[From R.F. Weiss (1970). Temp °C, temperature in degrees Celsius; salinity correction factors at 30 to 35 degrees Celsius are shown at the end of this table]

Temp	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
°C	0	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000	15000	16000
0.0	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.969	0.965	0.961	0.957	0.953	0.950	0.946	0.942	0.938
1.0	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.969	0.965	0.962	0.958	0.954	0.950	0.946	0.942	0.938
2.0	1.000	0.996	0.992	0.989	0.985	0.981	0.977	0.973	0.970	0.966	0.962	0.958	0.954	0.950	0.946	0.942	0.938
3.0	1.000	0.996	0.993	0.989	0.985	0.981	0.977	0.974	0.970	0.966	0.962	0.958	0.954	0.951	0.947	0.943	0.939
4.0	1.000	0.996	0.993	0.989	0.985	0.981	0.978	0.974	0.970	0.966	0.962	0.959	0.955	0.951	0.947	0.943	0.939
5.0	1.000	0.996	0.993	0.989	0.985	0.981	0.978	0.974	0.970	0.966	0.963	0.959	0.955	0.951	0.947	0.944	0.940
6.0	1.000	0.996	0.993	0.989	0.985	0.982	0.978	0.974	0.970	0.967	0.963	0.959	0.955	0.952	0.948	0.944	0.940
7.0	1.000	0.996	0.993	0.989	0.985	0.982	0.978	0.974	0.971	0.967	0.963	0.959	0.956	0.952	0.948	0.944	0.941
8.0	1.000	0.996	0.993	0.989	0.986	0.982	0.978	0.975	0.971	0.967	0.963	0.960	0.956	0.952	0.949	0.945	0.941
9.0	1.000	0.996	0.993	0.989	0.986	0.982	0.978	0.975	0.971	0.967	0.964	0.960	0.956	0.953	0.949	0.945	0.941
10.0	1.000	0.996	0.993	0.989	0.986	0.982	0.979	0.975	0.971	0.968	0.964	0.960	0.957	0.953	0.949	0.946	0.942
11.0	1.000	0.996	0.993	0.989	0.986	0.982	0.979	0.975	0.971	0.968	0.964	0.961	0.957	0.953	0.950	0.946	0.942
12.0	1.000	0.997	0.993	0.989	0.986	0.982	0.979	0.975	0.972	0.968	0.965	0.961	0.957	0.954	0.950	0.946	0.943
13.0	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.975	0.972	0.968	0.965	0.961	0.958	0.954	0.950	0.947	0.943
14.0	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972	0.969	0.965	0.961	0.958	0.954	0.951	0.947	0.943
15.0	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972	0.969	0.965	0.962	0.958	0.955	0.951	0.947	0.944
16.0	1.000	0.997	0.993	0.990	0.986	0.983	0.979	0.976	0.972	0.969	0.966	0.962	0.958	0.955	0.951	0.948	0.944
17.0	1.000	0.997	0.993	0.990	0.986	0.983	0.980	0.976	0.973	0.969	0.966	0.962	0.959	0.955	0.952	0.948	0.945
18.0	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.976	0.973	0.969	0.966	0.963	0.959	0.956	0.952	0.949	0.945
19.0	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.976	0.973	0.970	0.966	0.963	0.959	0.956	0.952	0.949	0.945
20.0	1.000	0.997	0.993	0.990	0.987	0.983	0.980	0.977	0.973	0.970	0.966	0.963	0.960	0.956	0.953	0.949	0.946
21.0	1.000	0.997	0.993	0.990	0.987	0.984	0.980	0.977	0.973	0.970	0.967	0.963	0.960	0.957	0.953	0.950	0.946
22.0	1.000	0.997	0.993	0.990	0.987	0.984	0.980	0.977	0.974	0.970	0.967	0.964	0.960	0.957	0.953	0.950	0.947
23.0	1.000	0.997	0.994	0.990	0.987	0.984	0.980	0.977	0.974	0.971	0.967	0.964	0.960	0.957	0.954	0.950	0.947
24.0	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.977	0.974	0.971	0.967	0.964	0.961	0.957	0.954	0.951	0.947
25.0	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.977	0.974	0.971	0.968	0.964	0.961	0.958	0.954	0.951	0.948
26.0	1.000	0.997	0.994	0.990	0.987	0.984	0.981	0.978	0.974	0.971	0.968	0.965	0.961	0.958	0.955	0.951	0.948
27.0	1.000	0.997	0.994	0.991	0.987	0.984	0.981	0.978	0.975	0.971	0.968	0.965	0.962	0.958	0.955	0.952	0.948
28.0	1.000	0.997	0.994	0.991	0.987	0.984	0.981	0.978	0.975	0.972	0.968	0.965	0.962	0.959	0.955	0.952	0.949
29.0	1.000	0.997	0.994	0.991	0.988	0.984	0.981	0.978	0.975	0.972	0.969	0.965	0.962	0.959	0.956	0.952	0.949

Table 6.2–7. Salinity correction factors for dissolved oxygen in water (based on conductivity)—Continued

Temp	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
°C	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000	30000	31000	32000	33000
0.0	0.934	0.930	0.926	0.922	0.918	0.914	0.910	0.905	0.901	0.897	0.893	0.889	0.885	0.881	0.877	0.873	0.869
1.0	0.934	0.930	0.926	0.922	0.918	0.914	0.910	0.906	0.902	0.898	0.894	0.890	0.886	0.882	0.878	0.874	0.870
2.0	0.935	0.931	0.927	0.923	0.919	0.915	0.911	0.907	0.903	0.899	0.895	0.891	0.887	0.883	0.879	0.875	0.871
3.0	0.935	0.931	0.927	0.923	0.919	0.915	0.911	0.907	0.903	0.899	0.895	0.891	0.887	0.883	0.879	0.875	0.871
4.0	0.935	0.932	0.928	0.924	0.920	0.916	0.912	0.908	0.904	0.900	0.896	0.892	0.888	0.884	0.880	0.876	0.872
5.0	0.936	0.932	0.928	0.924	0.920	0.917	0.913	0.909	0.905	0.901	0.897	0.893	0.889	0.885	0.881	0.877	0.873
6.0	0.936	0.933	0.929	0.925	0.921	0.917	0.913	0.909	0.905	0.902	0.898	0.894	0.890	0.886	0.882	0.878	0.874
7.0	0.937	0.933	0.929	0.925	0.922	0.918	0.914	0.910	0.906	0.902	0.898	0.894	0.891	0.887	0.883	0.879	0.875
8.0	0.937	0.933	0.930	0.926	0.922	0.918	0.914	0.911	0.907	0.903	0.899	0.895	0.891	0.887	0.884	0.880	0.876
9.0	0.938	0.934	0.930	0.926	0.923	0.919	0.915	0.911	0.907	0.904	0.900	0.896	0.892	0.888	0.884	0.880	0.877
10.0	0.938	0.934	0.931	0.927	0.923	0.919	0.916	0.912	0.908	0.904	0.900	0.897	0.893	0.889	0.885	0.881	0.877
11.0	0.939	0.935	0.931	0.927	0.924	0.920	0.916	0.912	0.909	0.905	0.901	0.897	0.894	0.890	0.886	0.882	0.878
12.0	0.939	0.935	0.932	0.928	0.924	0.920	0.917	0.913	0.909	0.906	0.902	0.898	0.894	0.890	0.887	0.883	0.879
13.0	0.939	0.936	0.932	0.928	0.925	0.921	0.917	0.914	0.910	0.906	0.902	0.899	0.895	0.891	0.887	0.884	0.880
14.0	0.940	0.936	0.933	0.929	0.925	0.922	0.918	0.914	0.911	0.907	0.903	0.899	0.896	0.892	0.888	0.884	0.881
15.0	0.940	0.937	0.933	0.929	0.926	0.922	0.918	0.915	0.911	0.907	0.904	0.900	0.896	0.893	0.889	0.885	0.882
16.0	0.941	0.937	0.934	0.930	0.926	0.923	0.919	0.915	0.912	0.908	0.904	0.901	0.897	0.893	0.890	0.886	0.882
17.0	0.941	0.938	0.934	0.930	0.927	0.923	0.920	0.916	0.912	0.909	0.905	0.901	0.898	0.894	0.891	0.887	0.883
18.0	0.942	0.938	0.934	0.931	0.927	0.924	0.920	0.917	0.913	0.909	0.906	0.902	0.899	0.895	0.891	0.888	0.884
19.0	0.942	0.938	0.935	0.931	0.928	0.924	0.921	0.917	0.914	0.910	0.906	0.903	0.899	0.896	0.892	0.888	0.885
20.0	0.942	0.939	0.935	0.932	0.928	0.925	0.921	0.918	0.914	0.911	0.907	0.903	0.900	0.896	0.893	0.889	0.886
21.0	0.943	0.939	0.936	0.932	0.929	0.925	0.922	0.918	0.915	0.911	0.908	0.904	0.901	0.897	0.893	0.890	0.886
22.0	0.943	0.940	0.936	0.933	0.929	0.926	0.922	0.919	0.915	0.912	0.908	0.905	0.901	0.898	0.894	0.891	0.887
23.0	0.944	0.940	0.937	0.933	0.930	0.926	0.923	0.919	0.916	0.912	0.909	0.905	0.902	0.898	0.895	0.891	0.888
24.0	0.944	0.941	0.937	0.934	0.930	0.927	0.923	0.920	0.917	0.913	0.910	0.906	0.903	0.899	0.896	0.892	0.889
25.0	0.944	0.941	0.938	0.934	0.931	0.927	0.924	0.921	0.917	0.914	0.910	0.907	0.903	0.900	0.896	0.893	0.889
26.0	0.945	0.941	0.938	0.935	0.931	0.928	0.925	0.921	0.918	0.914	0.911	0.907	0.904	0.901	0.897	0.894	0.890
27.0	0.945	0.942	0.938	0.935	0.932	0.928	0.925	0.922	0.918	0.915	0.911	0.908	0.905	0.901	0.898	0.894	0.891
28.0	0.946	0.942	0.939	0.936	0.932	0.929	0.926	0.922	0.919	0.915	0.912	0.909	0.905	0.902	0.898	0.895	0.892
29.0	0.946	0.943	0.939	0.936	0.933	0.929	0.926	0.923	0.919	0.916	0.913	0.909	0.906	0.903	0.899	0.896	0.892

Table 6.2–7. Salinity correction factors for dissolved oxygen in water (based on conductivity)—Continued

Temp °C	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000	45000	46000	47000	48000	49000	50000
0.0	0.865	0.861	0.856	0.852	0.848	0.844	0.840	0.836	0.832	0.828	0.823	0.819	0.815	0.811	0.807	0.803	0.799
1.0	0.866	0.862	0.857	0.853	0.849	0.845	0.841	0.837	0.833	0.829	0.825	0.821	0.816	0.812	0.808	0.804	0.800
2.0	0.867	0.862	0.858	0.854	0.850	0.846	0.842	0.838	0.834	0.830	0.826	0.822	0.818	0.814	0.809	0.805	0.801
3.0	0.867	0.863	0.859	0.855	0.851	0.847	0.843	0.839	0.835	0.831	0.827	0.823	0.819	0.815	0.811	0.807	0.803
4.0	0.868	0.864	0.860	0.856	0.852	0.848	0.844	0.840	0.836	0.832	0.828	0.824	0.820	0.816	0.812	0.808	0.804
5.0	0.869	0.865	0.861	0.857	0.853	0.849	0.845	0.841	0.837	0.833	0.829	0.825	0.821	0.817	0.813	0.809	0.805
6.0	0.870	0.866	0.862	0.858	0.854	0.850	0.846	0.842	0.838	0.834	0.830	0.826	0.822	0.818	0.814	0.810	0.806
7.0	0.871	0.867	0.863	0.859	0.855	0.851	0.847	0.843	0.839	0.835	0.831	0.828	0.824	0.820	0.816	0.812	0.808
8.0	0.872	0.868	0.864	0.860	0.856	0.852	0.848	0.844	0.840	0.837	0.833	0.829	0.825	0.821	0.817	0.813	0.809
9.0	0.873	0.869	0.865	0.861	0.857	0.853	0.849	0.845	0.842	0.838	0.834	0.830	0.826	0.822	0.818	0.814	0.810
10.0	0.874	0.870	0.866	0.862	0.858	0.854	0.850	0.846	0.843	0.839	0.835	0.831	0.827	0.823	0.819	0.815	0.811
11.0	0.874	0.871	0.867	0.863	0.859	0.855	0.851	0.848	0.844	0.840	0.836	0.832	0.828	0.824	0.820	0.817	0.813
12.0	0.875	0.871	0.868	0.864	0.860	0.856	0.852	0.849	0.845	0.841	0.837	0.833	0.829	0.825	0.822	0.818	0.814
13.0	0.876	0.872	0.869	0.865	0.861	0.857	0.853	0.850	0.846	0.842	0.838	0.834	0.830	0.827	0.823	0.819	0.815
14.0	0.877	0.873	0.869	0.866	0.862	0.858	0.854	0.851	0.847	0.843	0.839	0.835	0.832	0.828	0.824	0.820	0.816
15.0	0.878	0.874	0.870	0.867	0.863	0.859	0.855	0.852	0.848	0.844	0.840	0.836	0.833	0.829	0.825	0.821	0.817
16.0	0.879	0.875	0.871	0.867	0.864	0.860	0.856	0.853	0.849	0.845	0.841	0.838	0.834	0.830	0.826	0.822	0.819
17.0	0.879	0.876	0.872	0.868	0.865	0.861	0.857	0.854	0.850	0.846	0.842	0.839	0.835	0.831	0.827	0.824	0.820
18.0	0.880	0.877	0.873	0.869	0.866	0.862	0.858	0.855	0.851	0.847	0.843	0.840	0.836	0.832	0.829	0.825	0.821
19.0	0.881	0.877	0.874	0.870	0.867	0.863	0.859	0.855	0.852	0.848	0.844	0.841	0.837	0.833	0.830	0.826	0.822
20.0	0.882	0.878	0.875	0.871	0.867	0.864	0.860	0.856	0.853	0.849	0.845	0.842	0.838	0.834	0.831	0.827	0.823
21.0	0.883	0.879	0.876	0.872	0.868	0.865	0.861	0.857	0.854	0.850	0.846	0.843	0.839	0.836	0.832	0.828	0.825
22.0	0.884	0.880	0.876	0.873	0.869	0.866	0.862	0.858	0.855	0.851	0.848	0.844	0.840	0.837	0.833	0.829	0.826
23.0	0.884	0.881	0.877	0.874	0.870	0.866	0.863	0.859	0.856	0.852	0.849	0.845	0.841	0.838	0.834	0.830	0.827
24.0	0.885	0.882	0.878	0.874	0.871	0.867	0.864	0.860	0.857	0.853	0.850	0.846	0.842	0.839	0.835	0.832	0.828
25.0	0.886	0.882	0.879	0.875	0.872	0.868	0.865	0.861	0.858	0.854	0.851	0.847	0.843	0.840	0.836	0.833	0.829
26.0	0.887	0.883	0.880	0.876	0.873	0.869	0.866	0.862	0.859	0.855	0.852	0.848	0.844	0.841	0.837	0.834	0.830
27.0	0.887	0.884	0.880	0.877	0.874	0.870	0.867	0.863	0.860	0.856	0.853	0.849	0.845	0.842	0.838	0.835	0.831
28.0	0.888	0.885	0.881	0.878	0.874	0.871	0.867	0.864	0.860	0.857	0.853	0.850	0.846	0.843	0.839	0.836	0.832
29.0	0.889	0.886	0.882	0.879	0.875	0.872	0.868	0.865	0.861	0.858	0.854	0.851	0.848	0.844	0.841	0.837	0.834

Table 6.2–7. Salinity correction factors for dissolved oxygen in water (based on conductivity)—Continued

Temp	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
°C	51000	52000	53000	54000	55000	56000	57000	58000	59000	60000	61000	62000	63000	64000	65000	66000	67000
0.0	0.795	0.790	0.786	0.782	0.778	0.774	0.770	0.766	0.761	0.757	0.753	0.749	0.745	0.741	0.737	0.732	0.728
1.0	0.796	0.792	0.788	0.783	0.779	0.775	0.771	0.767	0.763	0.759	0.755	0.751	0.746	0.742	0.738	0.734	0.730
2.0	0.797	0.793	0.789	0.785	0.781	0.777	0.773	0.768	0.764	0.760	0.756	0.752	0.748	0.744	0.740	0.736	0.732
3.0	0.798	0.794	0.790	0.786	0.782	0.778	0.774	0.770	0.766	0.762	0.758	0.754	0.750	0.746	0.741	0.737	0.733
4.0	0.800	0.796	0.792	0.788	0.784	0.780	0.775	0.771	0.767	0.763	0.759	0.755	0.751	0.747	0.743	0.739	0.735
5.0	0.801	0.797	0.793	0.789	0.785	0.781	0.777	0.773	0.769	0.765	0.761	0.757	0.753	0.749	0.745	0.741	0.737
6.0	0.802	0.798	0.794	0.790	0.786	0.782	0.778	0.774	0.770	0.766	0.762	0.758	0.754	0.750	0.746	0.742	0.738
7.0	0.804	0.800	0.796	0.792	0.788	0.784	0.780	0.776	0.772	0.768	0.764	0.760	0.756	0.752	0.748	0.744	0.740
8.0	0.805	0.801	0.797	0.793	0.789	0.785	0.781	0.777	0.773	0.769	0.765	0.761	0.757	0.753	0.749	0.745	0.742
9.0	0.806	0.802	0.798	0.794	0.790	0.787	0.783	0.779	0.775	0.771	0.767	0.763	0.759	0.755	0.751	0.747	0.743
10.0	0.807	0.804	0.800	0.796	0.792	0.788	0.784	0.780	0.776	0.772	0.768	0.764	0.760	0.757	0.753	0.749	0.745
11.0	0.809	0.805	0.801	0.797	0.793	0.789	0.785	0.781	0.778	0.774	0.770	0.766	0.762	0.758	0.754	0.750	0.746
12.0	0.810	0.806	0.802	0.798	0.794	0.791	0.787	0.783	0.779	0.775	0.771	0.767	0.763	0.760	0.756	0.752	0.748
13.0	0.811	0.807	0.804	0.800	0.796	0.792	0.788	0.784	0.780	0.777	0.773	0.769	0.765	0.761	0.757	0.753	0.750
14.0	0.812	0.809	0.805	0.801	0.797	0.793	0.789	0.786	0.782	0.778	0.774	0.770	0.766	0.763	0.759	0.755	0.751
15.0	0.814	0.810	0.806	0.802	0.798	0.795	0.791	0.787	0.783	0.779	0.776	0.772	0.768	0.764	0.760	0.756	0.753
16.0	0.815	0.811	0.807	0.804	0.800	0.796	0.792	0.788	0.785	0.781	0.777	0.773	0.769	0.766	0.762	0.758	0.754
17.0	0.816	0.812	0.809	0.805	0.801	0.797	0.794	0.790	0.786	0.782	0.778	0.775	0.771	0.767	0.763	0.760	0.756
18.0	0.817	0.814	0.810	0.806	0.802	0.799	0.795	0.791	0.787	0.784	0.780	0.776	0.772	0.769	0.765	0.761	0.757
19.0	0.819	0.815	0.811	0.807	0.804	0.800	0.796	0.792	0.789	0.785	0.781	0.777	0.774	0.770	0.766	0.763	0.759
20.0	0.820	0.816	0.812	0.809	0.805	0.801	0.797	0.794	0.790	0.786	0.783	0.779	0.775	0.771	0.768	0.764	0.760
21.0	0.821	0.817	0.814	0.810	0.806	0.802	0.799	0.795	0.791	0.788	0.784	0.780	0.777	0.773	0.769	0.766	0.762
22.0	0.822	0.818	0.815	0.811	0.807	0.804	0.800	0.796	0.793	0.789	0.785	0.782	0.778	0.774	0.771	0.767	0.763
23.0	0.823	0.820	0.816	0.812	0.809	0.805	0.801	0.798	0.794	0.790	0.787	0.783	0.779	0.776	0.772	0.768	0.765
24.0	0.824	0.821	0.817	0.814	0.810	0.806	0.803	0.799	0.795	0.792	0.788	0.785	0.781	0.777	0.774	0.770	0.766
25.0	0.826	0.822	0.818	0.815	0.811	0.808	0.804	0.800	0.797	0.793	0.789	0.786	0.782	0.779	0.775	0.771	0.768
26.0	0.827	0.823	0.820	0.816	0.812	0.809	0.805	0.802	0.798	0.794	0.791	0.787	0.784	0.780	0.776	0.773	0.769
27.0	0.828	0.824	0.821	0.817	0.814	0.810	0.806	0.803	0.799	0.796	0.792	0.789	0.785	0.781	0.778	0.774	0.771
28.0	0.829	0.825	0.822	0.818	0.815	0.811	0.808	0.804	0.801	0.797	0.794	0.790	0.786	0.783	0.779	0.776	0.772
29.0	0.830	0.827	0.823	0.820	0.816	0.812	0.809	0.805	0.802	0.798	0.795	0.791	0.788	0.784	0.781	0.777	0.774

Table 6.2–7. Salinity correction factors for dissolved oxygen in water (based on conductivity)—Continued

Temp	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
°C	0	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000	15000	16000
30.0	1.000	0.997	0.994	0.991	0.988	0.985	0.981	0.978	0.975	0.972	0.969	0.966	0.962	0.959	0.956	0.953	0.950
31.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.978	0.975	0.972	0.969	0.966	0.963	0.959	0.956	0.953	0.950
32.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.979	0.975	0.972	0.969	0.966	0.963	0.960	0.957	0.953	0.950
33.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.979	0.976	0.973	0.969	0.966	0.963	0.960	0.957	0.954	0.951
34.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.979	0.976	0.973	0.970	0.967	0.963	0.960	0.957	0.954	0.951
35.0	1.000	0.997	0.994	0.991	0.988	0.985	0.982	0.979	0.976	0.973	0.970	0.967	0.964	0.961	0.957	0.954	0.951

Temp	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
°C	17000	18000	19000	20000	21000	22000	23000	24000	25000	26000	27000	28000	29000	30000	31000	32000	33000
30.0	0.946	0.943	0.940	0.936	0.933	0.930	0.927	0.923	0.920	0.917	0.913	0.910	0.907	0.903	0.900	0.896	0.893
31.0	0.947	0.943	0.940	0.937	0.934	0.930	0.927	0.924	0.920	0.917	0.914	0.911	0.907	0.904	0.901	0.897	0.894
32.0	0.947	0.944	0.941	0.937	0.934	0.931	0.928	0.924	0.921	0.918	0.914	0.911	0.908	0.905	0.901	0.898	0.895
33.0	0.947	0.944	0.941	0.938	0.935	0.931	0.928	0.925	0.922	0.918	0.915	0.912	0.908	0.905	0.902	0.899	0.895
34.0	0.948	0.945	0.941	0.938	0.935	0.932	0.929	0.925	0.922	0.919	0.916	0.912	0.909	0.906	0.903	0.899	0.896
35.0	0.948	0.945	0.942	0.939	0.935	0.932	0.929	0.926	0.923	0.919	0.916	0.913	0.910	0.906	0.903	0.900	0.897

Temp	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
°C	34000	35000	36000	37000	38000	39000	40000	41000	42000	43000	44000	45000	46000	47000	48000	49000	50000
30.0	0.890	0.886	0.883	0.879	0.876	0.873	0.869	0.866	0.862	0.859	0.855	0.852	0.849	0.845	0.842	0.838	0.835
31.0	0.890	0.887	0.884	0.880	0.877	0.873	0.870	0.867	0.863	0.860	0.856	0.853	0.850	0.846	0.843	0.839	0.836
32.0	0.891	0.888	0.884	0.881	0.878	0.874	0.871	0.868	0.864	0.861	0.857	0.854	0.851	0.847	0.844	0.840	0.837
33.0	0.892	0.889	0.885	0.882	0.879	0.875	0.872	0.868	0.865	0.862	0.858	0.855	0.851	0.848	0.845	0.841	0.838
34.0	0.893	0.889	0.886	0.883	0.879	0.876	0.873	0.869	0.866	0.863	0.859	0.856	0.852	0.849	0.846	0.842	0.839
35.0	0.893	0.890	0.887	0.883	0.880	0.877	0.874	0.870	0.867	0.863	0.860	0.857	0.853	0.850	0.847	0.843	0.840

Temp	Conductivity, in microsiemens per centimeter at 25 degrees Celsius																
°C	51000	52000	53000	54000	55000	56000	57000	58000	59000	60000	61000	62000	63000	64000	65000	66000	67000
30.0	0.831	0.828	0.824	0.821	0.817	0.814	0.810	0.807	0.803	0.800	0.796	0.793	0.789	0.786	0.782	0.779	0.775
31.0	0.832	0.829	0.825	0.822	0.818	0.815	0.811	0.808	0.804	0.801	0.797	0.794	0.790	0.787	0.783	0.780	0.776
32.0	0.833	0.830	0.826	0.823	0.820	0.816	0.813	0.809	0.806	0.802	0.799	0.795	0.792	0.788	0.785	0.781	0.778
33.0	0.834	0.831	0.828	0.824	0.821	0.817	0.814	0.810	0.807	0.803	0.800	0.797	0.793	0.790	0.786	0.783	0.779
34.0	0.836	0.832	0.829	0.825	0.822	0.818	0.815	0.812	0.808	0.805	0.801	0.798	0.794	0.791	0.788	0.784	0.781
35.0	0.837	0.833	0.830	0.826	0.823	0.820	0.816	0.813	0.809	0.806	0.803	0.799	0.796	0.792	0.789	0.785	0.782

SELECTED REFERENCES

American Public Health Association, 2005, Standard methods for the examination of water and wastewater (21st ed.): Washington, D.C., American Public Health Association, American Water Works Association, and Water Environment Federation, p. 4-136 to 4-137, http://www.standardmethods.org/.

ASTM International, 2006, D888-05 standard test methods for dissolved oxygen in water: accessed May 17, 2006, at http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/REDLINE_PAGES/D888.htm?L+mystore+zmtx1699.

ASTM International, 2005, D5543-94 (2005) standard test methods for low-level dissolved oxygen in water: accessed May 15, 2006, at http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/REDLINE_PAGES/D5543.htm?L+mystore+aaam0310.

Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, p. 126-129.

CHEMetrics, Inc., 2006, Oxygen, dissolved: accessed May 15, 2006, from http://www.chemetrics.com/catalogpdfs.html.

Gilbert, T.W., Behymer, T.D., Castaneda, H.B., March 1982, Determination of dissolved oxygen in natural and wastewaters: American Laboratory, p. 119-134.

Hach Company, Hach LDO technology—real-world FAQ: accessed September 27, 2005 at http://www.hach.com/hc/view.document.only.invoker/View=HTML_LDO_REALWORLD_FAQ/NewLinkLabel=Hach+LDO+Technology:+Real-World+FAQ/PREVIOUS_BREADCRUMB_ID=HC_SEARCH_KEYWORD/SESSIONID|ATBwTU1URXlOemMwTmpVek9UazJNeVpuZFdWemRFVldXQT09QQ==|.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 155-156.

In-Situ Inc., Multi-parameter water quality Troll®9500, accessed April 29, 2006 at http://www.in-situ.com/In-Situ/Products/TROLL9500/TROLL9500.html.

Kane, J.A., Improved optical sensor for monitoring dissolved oxygen, in NASA Tech Briefs, KSC-11998, accessed September 27, 2005, at http://www.nasatech.com/Briefs/Nov99/KSC11998.html.

Skougstad, M.W., Fishman, M.J., Friedman, L.C., Erdmann, D.E., and Duncan, S.S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 626 p.

U.S. Geological Survey, 1979, Analytical methods—recommended procedures for calibrating dissolved oxygen meters: Quality of Water Branch Technical Memorandum 79.10, accessed March 17, 2006, at http://water.usgs.gov/admin/memo/QW/qw79.10.html.

U.S. Geological Survey, 1981, Water quality—new tables of dissolved oxygen saturation values: Quality of Water Branch Technical Memorandum 81,11, accessed March 17, 2006, at http://water.usgs.gov/admin/memo/QW/qw81.11.html.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, available online at http://pubs.water.usgs.gov/twri9A.

Wagner, R.J., Boulger, Jr., R.W., Oblinger, C.J., and Smith, B.A., 2006, Guidelines and standard procedures for continuous water-quality monitors — station operation, record computation, and data reporting: U.S. Geological Survey Techniques and Methods 1-D3, available online only at http://pubs.water.usgs.gov/tm1D3.

Weiss, R.F., 1970, The solubility of nitrogen, oxygen and argon in water and seawater: Deep Sea Research, v. 17, p. 721–735.

White, A.F., Peterson, M.L., and Solbau, R.D., 1990, Measurement and interpretation of low levels of dissolved oxygen in ground water: Ground Water, v. 28, no. 4, p. 584–590.

Wood, W.W., 1981, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, p. 22-24.

ACKNOWLEDGMENTS

This *National Field Manual* responds to advances in technology and science and to the developing needs for water-quality monitoring. Its aim is to provide scientifically sound guidance to USGS personnel and to document USGS requirements for collecting water-quality data. As a result, the expertise of numerous scientists has been tapped in developing this manual and keeping it current. A great debt of gratitude is owed to the following original authors, editors, and reviewers of Chapter A6, Section 6.2 of this field manual: E.A. Ciganovich, I.M. Collies, J.V. Davis, C.M. Eberle, R.T. Iwatsubo, B.B. Palcsak, K.A. Pearsall, D.B. Radtke, D.A. Sherwood, A.H. Welch, F.D. Wilde, A.E. White, Chester Zenone, and the analysts of the USGS National Water Quality Laboratory.

Improvements to the technical quality of this revision to Section 6.2, Dissolved Oxygen, can be attributed to the expertise and conscientious efforts of technical reviewers Jacob Gibs, J.A. Kingsbury, and S.C. Skrobialowski. Special appreciation is extended to the scientists from the Hach, In-Situ Inc., and YSI Inc. companies, who were generous with their time and expertise in explaining luminescent-sensor technology. The editorial and production quality of this report is a credit to I.M. Collies and L.J. Ulibarri. Thanks go to F.D. Wilde, managing editor of the *National Field Manual*, for maintaining the integrity of the technical and publication process.

TURBIDITY 6.7

By Chauncey W. Anderson

Illustrations

Tables

TURBIDITY 6.7

Turbidity, which can make water appear cloudy or muddy, is caused by the presence of suspended and dissolved matter, such as clay, silt, finely divided organic matter, plankton and other microscopic organisms, organic acids, and dyes (ASTM International, 2003a). The color of water, whether resulting from dissolved compounds or suspended particles, can affect a turbidity measurement.

TURBIDITY–an expression of the optical properties of a liquid that causes light rays to be scattered and absorbed rather than transmitted in straight lines through a sample.

— ASTM, 2003a

Although turbidity is not an inherent property of water, as is temperature or pH (Davies-Colley and Smith, 2001), the recognition of turbidity as an indicator of the environmental health of water bodies has increased over the past decade, resulting in a growing demand for high-quality and objective turbidity measurements. To meet this demand, relatively inexpensive, yet sophisticated instruments have been developed that allow for nearly continuous monitoring and data logging of turbidity in natural waters. Gray and Glysson (2003) note the following examples of disparate uses for turbidity data:

- Regulating and maintaining drinking water clarity.
- Determining water clarity for aquatic organisms.
- Indicating visual impairment in water.
- Real-time monitoring that indicates watershed conditions.
- Developing surrogates for concentration of suspended sediment (SSC) and other constituents.
- Monitoring the effects of land development and related human activities and subsequent management of natural resources.
- Determining transport of contaminants associated with suspended materials.

Although technological advances in turbidity measurement have produced a variety of instrument types to meet one or more of these differing objectives, turbidity instruments of different designs commonly do not yield identical or equivalent results. Moreover, the mixing of different source waters or dilutions of environmental samples may not produce linear results when measuring for turbidity because of the variety of factors that contribute to and can have an effect on turbidity. Selection of the appropriate turbidity instrument requires, therefore, consideration of project objectives, data requirements, and the physical and chemical properties of the water body.

This section on turbidity provides protocols and guidelines for selecting appropriate field and laboratory instruments and procedures for instrument calibration and maintenance, turbidity measurement, data storage, and quality assurance that meet stated objectives for U.S. Geological Survey (USGS) data-collection efforts.[1] The use of consistent procedures and instruments within and among projects or programs for which turbidity data will be compared over space and time is crucial for the the success of the data-collection program.

Select instruments carefully after reviewing project objectives and after consulting with cooperating agencies.

- **Report turbidity on the basis of the individual instrument design.**
- **Use identically prepared calibration solutions.**
- **Use consistent techniques and instrumentation throughout a data-collection program.**

[1]For additional procedures related to continuous, dynamic monitoring of environmental waters, refer to Wagner and others (2000).

EQUIPMENT 6.7.1

When selecting an appropriate instrument for measuring turbidity, consider the potential effects that may result from the various properties of different water bodies. In addition, ensure that the measurement method, instrument design, and the data output are appropriate for the purpose and objectives for which these data are to be collected.

INTERFERENCES AND INSTRUMENT DESIGN 6.7.1.A

A variety of water properties can affect the measurement of turbidity (table 6.7-1). These include the color of dissolved constituents in the water matrix and particulate materials, particle size, and density. Sensor fouling, such as biological growth or scratches on the optical surface of the instrument, tends to produce a negative bias when light beams are blocked, but can produce a positive bias if scratches increase the scatter of the sensor's light beam (table 6.7-2). Likewise, bubbles or gases in the water can cause apparent turbidity (positive bias), and might require special sample preparation or handling to eliminate without changing the particle characteristics of the original sample (consult manufacturer’s recommendations).

To account for the effects of properties of water or interferences on turbidity, many types of instruments have been designed (table 6.7-3), many with multiple light beams or detectors (fig. 6.7-1). For example, although stray light can cause a positive bias in turbidity measurement because of apparent additional reflectance, many newer instruments, particularly those used for dynamic monitoring, are designed to minimize stray light.

For a valid comparison of turbidity data over time, between sites, and among projects, use instruments with identical optical and data-processing configurations.

Table 6.7-1. Properties of water matrices and their expected effect on turbidity measurement

[Negative, a negative effect produces a disproportionately low measurement; IR, infrared; nm, nanometers; positive, a positive effect produces a disproportionately high measurement; ~, approximately. See table 6.7-3 for descriptions of instrument designs.]

Properties of water matrix	Effect on the measurement	Direction of effect on the measurement	Instrument designs to compensate for effect
Colored particles	Absorption of light beam	Negative	• Near IR (780-900 nm) light source • Multiple detectors
Color, dissolved (in the matrix)	Absorption of light beam (if the incident light wavelengths overlap the absorptive spectra within the sample matrix)	Negative	• Near IR (780-900 nm) light source • Multiple detectors
Particle size:	*Wavelength dependent.*		
Large particles	• Scatter long wavelengths of light more readily than small particles	• Positive (for near IR light source, ~820-900 nm)	• White light (broad spectrum) light source
Small particles	• Scatter short wavelengths of light more efficiently than long wavelengths	• Positive (for broad spectrum light source, such as white light)	• Near IR (780-900 nm) light source
Particle Density	Increases forward and backward scattering of light at high densities	Negative	• Multiple detectors • Backscattering

Table 6.7-2. Sampling interferences and their expected effect on turbidity measurement

[Positive, a positive effect produces a disproportionately high measurement; Negative, a negative effect produces a disproportionately low measurement.]

Interference	Effect on the measurement	Direction of effect on the measurement
Stray light	Increases apparent light scatter	Positive
Bubbles from entrained gases	Increases apparent light scatter	Positive
Contamination of calibrants	Increases apparent light scatter	Positive
Optical sensor fouling or scratching	*Particularly with dynamic instruments.* • Possible beam blockage • Possible scratches on optical surfaces	• Negative • Positive
Bubbles	Increases apparent light scatter	Positive
Scratches on cuvette glass	Increases apparent light scatter	Positive

Table 6.7-3. Summary of instrument designs and capabilities, current reproducible technologies, appropriate applications, and approximate limits

[Indicated ranges are for example only and do not exclude the possibility that manufacturers can develop instruments under each design that surpass these ranges. Abbreviations: EPA 180.1, U.S. Environmental Protection Agency (1993) method 180.1; Regulatory, range complies with EPA regulations (unless specified "non-US"); IR, infrared; ISO 7027, International Organization for Standardization (1999) method 7027; nm, nanometers; US, United States]

Design	Prominent feature and application	Typical instrument capability range (nm)	Suggested application range (nm)
Nephelometric non-ratiometric	White light turbidimeters – Complies with EPA 180.1 for low-level monitoring.	0 to 40	0 to 40 Regulatory
Ratiometric white-light turbidimeters	Complies with EPA 180.1 for low-level monitoring. Uses a nephelometric detector as the primary detector, but contains other detectors to minimize effects of color and noise. Can be used for both low- and high-level measurement.	0 to 4,000	0 to 40 Regulatory 0 to 4,000
Nephelometric, near-IR turbidimeters, non-ratiometric	Complies with ISO 7027 – The wavelength (780-900 nm) is less susceptible to effects of color. Good for samples with color and good for low-level monitoring.	0 to 1,000	0 to 11 Regulatory (non-US) 0 to 1,000
Nephelometric near-IR turbidimeters, ratiometric	Complies with ISO 7027. Contains a ratio algorithm to monitor and compensate for variability and color.	0 to 4,000	0 to 40 Regulatory 0 to 4,000
Surface-scatter turbidimeters	Not applicable for regulatory purposes. Turbidity is determined through light scatter from or near the surface of a sample. The detection angle is still nephelometric, but interferences are not as substantial as nephelometric non-ratiometric measurements. This is primarily used in high-level turbidity applications.	10 to 10,000	10 to 10,000
Backscatter/ ratiometric technology	Not applicable for regulatory purposes. Backscatter detection for high levels and nephelometric detection for low levels. Backscatter is common with probe technology and is best applied in high turbidity samples.	10 to 10,000	10 to 10,000
Light attenuation (spectro-photometric)	Not applicable for regulatory purposes. Wavelength 860 nm. Highly susceptible to interferences; best applied at low to medium turbidity levels.	20 to 1,000	20 to 1,000
Multiple-beam turbidimeters	Multiple light sources and multiple detectors are used to provide both reference and active signals, with at least four independent measurements being made. The final signal is determined with a ratio algorithm.	0 to 40	0 to 40 Regulatory 0 to 1,000

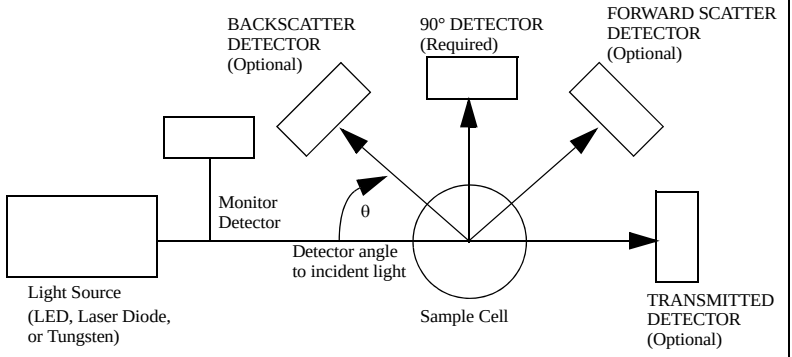


Figure 6.7-1. Photoelectric nephelometer (single-beam design) showing optional additional detectors for ratiometric, backscatter, or transmitted determination of turbidity. [Modified from Sadar (1998)].

One outcome of the availability of different instrument designs is that **turbidity measured using instruments with different optical designs can differ by factors of two or more for the same environmental sample, even with identically calibrated instruments**. Thus, raw data from differently designed instruments should not be considered directly interchangeable—the resultant data are inherently incomparable without additional work to establish relations between instruments over the range of the environmental conditions present.

Such complications underscore the need to clearly determine study objectives before selecting a turbidimeter, and to understand the limitations of the instrument selected. In addition, a carefully planned quality-assurance (QA) protocol is required to identify errors associated with different aspects of the turbidity measurement process. For additional information on turbidity measurement, see Sadar (1998), U.S. Environmental Protection Agency (1999), and the literature provided by instrument manufacturers.

TECHNICAL NOTE (1): Variability in measurements caused by instability in light sources, high particle densities, or color can be reduced by the use of multiple detectors at different angles. Such "ratiometric" instruments compute the turbidity value using a ratio of the light received by the different detectors. Furthermore, because turbidity is an optical measurement, the absorption of light by colored particles or by a colored matrix can cause a reduction in the apparent turbidity. The negative effect from color is minimized by using near-infrared light frequencies as the light source (tables 6.7-1, 6.7-3) or ratiometric techniques.

DATA STORAGE 6.7.1.B

To ensure that USGS turbidity data can be understood and interpreted properly within the context of the instrument used and site conditions encountered, data from each instrument type will be stored and reported in the National Water Information System (NWIS) using parameter codes and measurement reporting units that are specific to the instrument type, with specific instruments designated by the method code. The respective measurement units, most of which also are in use internationally, are listed and defined in table 6.7-4.

- The designations NTU, NTRU, BU, AU, and NTMU signify the use of a broad spectrum incident light in the wavelength range 400-680 nanometers (nm).
- The designations FNU, FNRU, FBU, FAU, and FNMU generally signify an incident light in the range between 780-900 nm.[2]

These reporting units are equivalent when measuring a calibration solution (for example, formazin or polymer beads—see section 6.7.2), but their respective instruments may not produce equivalent results for environmental samples. **Information for specific instruments is maintained at: http://water.usgs.gov/owq/turbidity_codes.xls**

The term "turbidity unit," as used in this manual, refers generically to turbidity measured by instruments of undefined design. Note that manufacturers might, for the foreseeable future, retain the general use of the measurement unit "NTU" when referring to calibrants and equipment.

> **TECHNICAL NOTE (2):** Historically, reporting units included Jackson Turbidity Units (JTU) and Formazin Turbidity Units (FTU). Neither unit is still in common use, due to lack of precision (JTU) and lack of specificity about instrumentation type (FTU).

[2]ISO 7027 specifically defines the light source for FNU measurements as having a wavelength of 860 nm, with a bandwidth of 60 nm. The angle of the detector must be 90 degrees from incident light, plus or minus 2.5 degrees.

Table 6.7-4. Reporting units corresponding to turbidity instrument designs

[Parameter code numbers begin with a "P"; nm, nanometers; °, degree; ±, plus or minus; K, kelvin]

Detector geometry	Light wavelength	
	White or broadband (with a peak spectral output of 400-680 nm)	Monochrome (spectral output typically near infrared, 780-900 nm)
Single illumination beam light source		
At 90° to incident beam	Nephelometric Turbidity Unit (NTU)[1] (P63675)	Formazin Nephelometric Unit (FNU)[2] (P63680)
At 90° and other angles. An instrument algorithm uses a combination of detector readings, which may differ for values of varying magnitude.	Nephelometric Turbidity Ratio Unit (NTRU) (P63676)	Formazin Nephelometric Ratio Unit (FNRU) (P63681)
At 30° ± 15 to incident beam (backscatter)	Backscatter Unit (BU) (P63677)	Formazin Backscatter Unit (FBU) (P63682)
At 180° to incident beam (attenuation)	Attenuation Unit (AU) (P63678)	Formazin Attenuation Unit (FAU) (P63683)
Multiple illumination beam light source		
At 90° and possibly other angles to each beam. An instrument algorithm uses a combination of detector readings, which may differ for values of varying magnitude.	Nephelometric Turbidity Multibeam Unit (NTMU) (P63679)	Formazin Nephelometric Multibeam Unit (FNMU) (P63684)

[1]EPA Method 180.1 defines the optical geometry for NTU measurements. The detector angle must be 90° ± 30 to the incident light beam. The light source must be a tungsten lamp with color temperature 2,200 - 3,000 K. (Source: U.S. Environmental Protection Agency, 1993)

[2]ISO 7027 defines the optical geometry for FNU measurements. The detector angle must be 90° ± 2.5 to the incident light beam. The light source must be a light-emitting diode (LED) with wavelength 860 ± 60 nm. (Source: International Organization for Standardization, 1999).

INSTRUMENT SELECTION AND MAINTENANCE 6.7.1.C

Owing to potential differences in turbidity readings resulting from different instrument types, it is critical that when selecting turbidimeters, investigators carefully consider the objectives of the study and the uses of the resulting data. Considerations include:

- Whether the program will be regulatory in nature (typically applies in a drinking water context).
- The expected range in turbidity and the portions of that range that will be the most important to measure with accuracy.
- The need for consistency of method and comparability among data sources (whether data from one site need to be comparable with data from another site or with historical data).
- Which potential interferences are the most important to quantify or otherwise take into account (tables 6.7-1 through 6.7-4).

Within the United States, turbidity is regulated by the U.S. Environmental Protection Agency (USEPA) only for water that is intended for use as drinking water. In some cases, States use turbidity for regulations associated with the Clean Water Act (U.S. Environmental Protection Agency, 2002a). To date, the USEPA has approved the following three methods to measure turbidity in drinking water: (1) EPA Method 180.1 (U.S. Environmental Protection Agency, 1993), based on white-light nephelometric instrument designs; (2) GLI Method 2 (U.S. Environmental Protection Agency, 1999; Great Lakes Instrument Company, undated), which uses a dual-beam and dual detector technology with an 860 nm light-emitting diode (LED) light source to compensate for color and reduce erratic readings; and (3) Hach Method 10133 (U.S. Environmental Protection Agency, 2002b), an inline process-stream method that is unlikely to be used within USGS. Owing to a nonlinear response of these technologies at high turbidities, their applicable range in drinking water is from 0 to 40 turbidity units. Instrument designs that conform to EPA Method 180.1 or GLI Method 2 may perform poorly (including nonlinear responses) at turbidities that commonly occur in surface-water bodies (greater than 40 turbidity units). Also, white-light instruments typically consume more power than monochrome instruments, so access to the regional power grid is commonly required. For these methods, waters with turbidities greater than 40

must be diluted before measuring. **For studies involving the measurement of turbidity in finished drinking water, either EPA Method 180.1, GLI Method 2, or Hach Method 10133 must be used**. (This requirement commonly is applied when determining ground-water turbidity in water from wells used for human consumption.)

> **TECHNICAL NOTE (3)**: One other method, ISO 7027 (International Organization for Standardization, 1999), has been defined for waters with low turbidity and is in use in Europe and elsewhere; however, as of 2003, ISO 7027 had not been accepted by USEPA for compliance with drinking-water regulations in the United States.

USEPA-approved methods generally are not required when providing data for regulatory purposes in accordance with the Clean Water Act (U.S. Environmental Protection Agency, 2002a). For example, nonregulatory methods can be used to determine changes in turbidity of surface water resulting from resource management actions, or to correlate turbidity with regulated constituents such as suspended sediment (Uhrich and Bragg, 2003), nutrients, or bacteria (Christensen and others, 2000). For such data-collection efforts, it may be possible to use alternative instrument designs that are targeted towards specific study objectives and that will accommodate the range of natural conditions that occur in the water body. **Before selecting a methodology and the corresponding instrumentation, determine if USEPA-compliant methodologies are necessary.** Given the breadth of applications for measuring turbidity, no particular sampling consideration can be defined as the most important in all cases; however, **consistency of instrument types and calibration procedures within monitoring programs or among individual projects is one of the most important aspects to consider when designing a data-collection program that will include turbidity.**

Nephelometry: the measurement of light scattering using a light detector 90 degrees from the incident light (USEPA, 1999).

Decision Considerations for Instrument Selection

Numerous factors are involved when deciding on the type(s) of equipment that are appropriate for a given study. A major consideration in the selection of a turbidity instrument is whether turbidity will be measured under **static** or **dynamic** conditions. Water samples that are removed from the source and are measured with benchtop meters are considered static. Submersible sensors allow turbidity measurement under dynamic water conditions, using either instantaneous profiling techniques or a deployed instrument for continuous monitoring.

Measurements taken under static conditions compared to those taken under dynamic conditions differ primarily because static-measurement techniques do not completely account for particle settling, whereas dynamic-measurement techniques more accurately reflect the dynamic nature of particle movement within the water body. Such differences are particularly pronounced when coarse silt or sand-sized particles are present. Also, temperature changes in the sample during transport from source water to laboratory can cause differences between measurements taken on a static sample (benchtop instrument) and measurements taken under dynamic (in situ or pumped) conditions. Some benchtop instruments do, however, provide flowthrough chambers that keep the sample in motion to approximate the dynamic conditions in the original water body.

As discussed previously, instrument selection begins with a thorough consideration of study objectives, and continues with questions about the use of the data, the type of water body and its sources of turbidity, and the way in which the data will be collected and stored. A decision tree (fig. 6.7-2) is provided below to help guide the selection process. In the decision process described below, numbers 1 through 3 pertain to information in fig. 6.7-2; numbers 4 and 5 provide additional guidance.

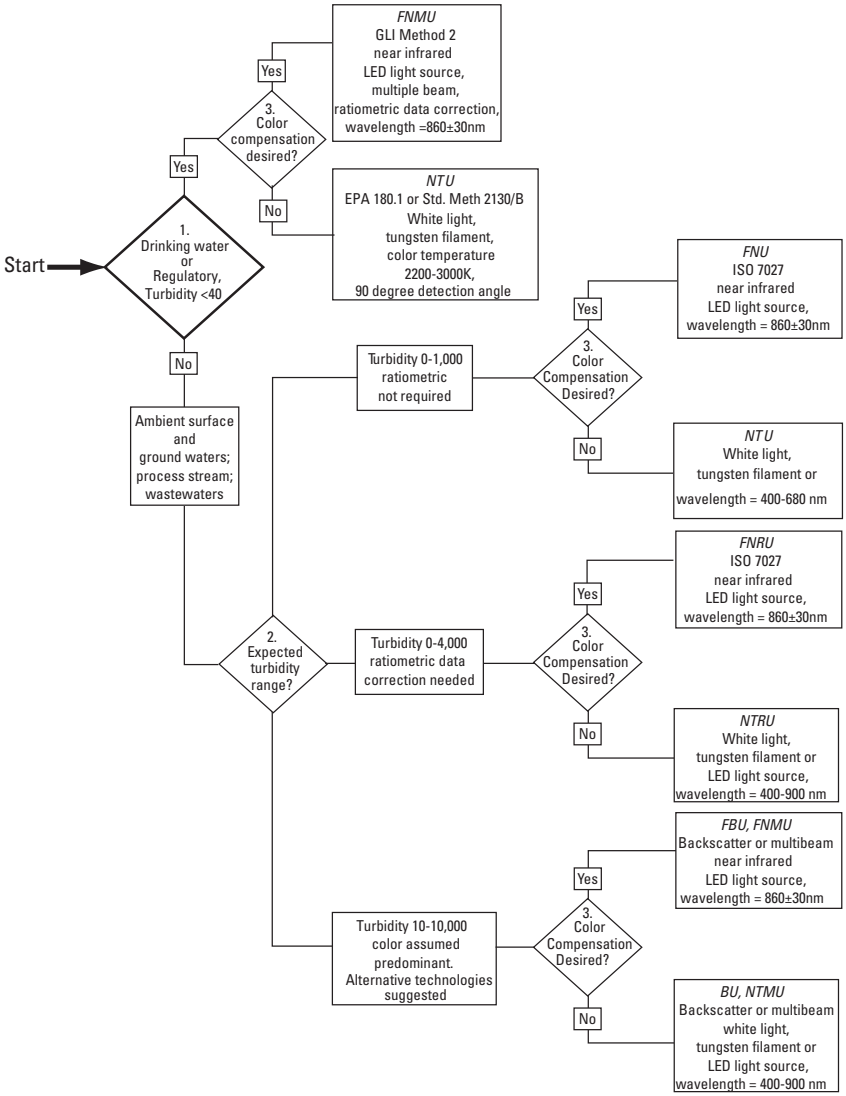


Figure 6.7-2. Decision tree to determine appropriate instrumentation designs for intended turbidity measurements.

Decision Considerations (considerations 4 and 5 are not shown in fig. 6.7-2)**:**

1. **Is the study regulatory in nature?**
   If "Yes," go to step **3 (**fig. 6.7-2).
   If "No," continue to step **2** (fig. 6.7-2).

   If the study involves regulation of drinking water, the instrument choices are limited by the methods accepted by the USEPA for drinking water. If the study involves State regulations (for example, those proposed under provisions of the Clean Water Act), the regulations may require the use of one or more specific instrument designs, which cannot be anticipated in this protocol.

   If the study does not involve turbidity in drinking water or other specially designated instrument types, consider using instrument designs that accommodate a broader range of environmental conditions.

2. **What is the expected range in turbidity, or what part of the range is most important to measure accurately?**

   For turbidities in the range of 0-1,000 units, single-detector nephelometric measurement may work adequately if the instrument is calibrated in the same range as the sample. As particle densities increase, however, the backward scattering of light particles increases to the point that it can cause interference with single-detector nephelometry, resulting in a negative effect on the measurement or an unstable reading (table 6.7-1). Multiple detectors at different angles can be used, with the turbidity value determined by a ratio of the light received by the different detectors. Ratioing helps to reduce noise in the turbidity signal, especially at ultra-low turbidities or when particle densities are high. Instruments that utilize backscatter detection also can help compensate for such effects at high turbidities. Backscatter is particularly important above 1,000 units. The effect of particle size should be considered too. Positive effects on turbidities for water sources with predominantly large or small particle sizes can be minimized with careful consideration of the study objectives, the water source, and instrument requirements.

3. Is the water source colored by dissolved or particulate materials, and should the color be part of the measured turbidity?

Color in water samples, from dissolved or particulate materials (or both), can cause a negative effect (Sutherland and others, 2000) on measured turbidity (table 6.7-1). In some cases, it could be desirable to quantify this decrease by using an instrument with a broad-spectrum or white-light source that would be sensitive to color changes. Alternatively, when measuring changes in turbidity that are unrelated to color, instruments with a near-infrared light source should be used.

4. Will the measurement be done by dynamic means or by a benchtop measurement of samples removed from the source?

In most cases, it is preferable to measure turbidity directly within the water source or in a pumped sample (dynamically), rather than taking a sample from which an aliquot must then be measured using a benchtop (static) method. Dynamic measurement is preferred to static measurement because of problems with representative subsampling, settling of solids and temperature changes in static samples, and interferences such as condensation or scratches on sample cuvettes. Dynamic techniques usually are required for continuous monitoring, and the sensors often can be combined with other sensors that measure additional properties, such as temperature, specific conductance, dissolved oxygen, and pH. In some cases, however, dynamic readings are not feasible or desired (for example, if a measurement is needed of a composite sample or in a laboratory setting). Most instruments used for static measurements are not capable of being used for dynamic measurements; whereas some instruments used for dynamic measurements can be immersed in a water sample and the measurement taken statically.

5. What resolution is required in the resulting data?

For turbidity data that primarily will be in the low (less than 5 turbidity units) or ultra-low (less than 1 unit) ranges, the necessary resolution may be down to the 100th or 10th decimal place, whereas for turbidities greater than 40 units, resolution to the nearest 5, 10, or even 100 reporting units might be adequate. After determining the primary instrument design requirements, consult literature or online sources of individual instrument manufacturers for information on available resolution.

Once a particular instrument design and set of reporting units (table 6.7-4) have been selected, the user evaluates the literature and cost information from instrument manufacturers to decide on the most appropriate model. Although rapid changes in optical and sensor technology preclude the inclusion of specific manufacturers' models in figure 6.7-2, the turbidity parameter and methods codes spreadsheet (http://water.usgs.gov/owq/turbidity_codes.xls, accessed 9/30/2005) provides a partial list of available models according to instrument design and reporting units, which can be used in combination with figure 6.7-2 to narrow the options for the choice of an instrument to meet a specific set of study objectives.

Figure 6.7-2 shows that differences among instrument designs have resulted in a wide array of options for measuring turbidity. Although these options provide flexibility and the capability to tailor the data-collection program to the needs of each particular study, they also present problems for data comparison among studies with differing objectives or water sources, particularly if different equipment is used in the studies. When data are to be compared among different programs or studies, sending duplicate samples to a laboratory such as the National Water Quality Laboratory (NWQL) provides a reference for quality-assurance purposes and is recommended (the NWQL, for example, simulates dynamic measurement using a flowthrough chamber with its benchtop meters). If a dynamic measurement is used for determining field turbidities, it can be useful to compare these data with results obtained from a laboratory-analyzed sample, as long as the properties contributing to the sample turbidity do not degrade during storage and transit (see section 6.7.3).

Dynamic measurement is the preferred method for determining the turbidity of a water body, provided that this method is consistent with study objectives and other study protocols. Dynamic measurement more accurately reflects surface-water conditions than static determination because particle settling in cuvettes is avoided.

Signal-Processing Options

Because turbidity measurements can be highly variable, a range of signal-processing options may be available with different instruments. Some instruments can provide statistics such as the maximum, minimum, mean, median, range, and variance of many readings over a timespan of a few seconds. These statistics can be useful for reducing variability in recorded turbidities, for understanding sources of turbidity, or for diagnostic purposes. Instruments that use proprietary algorithms can provide functions intended to reduce spikes in instantaneous data, sometimes employing user-defined variables such as time constants and spike thresholds. Such algorithms can provide a smoother signal than simple instantaneous measurements; however, because the algorithms may not be published, these data must be used with care and in consideration of the data-quality objectives of the study. Note that if the instrument uses signal averaging to smooth the data output, the instrument response to changes in turbidity readings can be slowed. **Select the output you desire in accordance with study objectives and data-storage and transmittal requirements.**

Maintenance of Turbidity Instruments

The equipment and supplies commonly used for field measurement of turbidity are listed in table 6.7-5. These include supplies generally needed for the maintenance, storage, and cleaning of the selected instrument. Routine maintenance of turbidity instrumentation is critical, particularly for continuously deployed, dynamic applications.

Table 6.7-5. Equipment and supplies used for measuring turbidity

[Modify this list to meet the specific needs of the field effort. Abbreviations: ≤, less than or equal to; mm, millimeter; mL, milliliter]

- Turbidimeter, spectrophotometer, or submersible-sensor instrument (such as a multiparameter instrument with a turbidity sensor).[1]
- Calibration turbidity stock solutions and standards
  - Formazin stock suspension, commercially obtained or prepared from scratch with hydrazine sulfate and hexamethelenetetramine chemicals, or
  - Instrument-specific polymer solutions containing styrene divinylbenzene beads.
- Sample cells (cuvettes), clear colorless glass (supplied from instrument manufacturer).
- Inert (dry) gas (for example, nitrogen) and gas-delivery apparatus; tanks must be fitted with regulators and filter.
- Sample bottle (preferably an amber bottle that does not sorb suspended material).
- Silicon oil, optical grade (with same index of refraction as sample cells; supplied by instrument manufacturer).
- Paper tissues, extra lint free.
- Turbidity-free water, deiononized water filtered through a ≤ 0.2 mm filter membrane with precision-sized pores.
- Bottle to hold turbidity-free water, cleaned and rinsed three times with filtered water.
- Volumetric flask, Class A, 100 mL or 500 mL.
- Volumetric pipet, Class A, 5.0 mL and pipet filler.

[1]See text, figure 6.7-2, and table 6.7-3 for description of appropriate instrument types.

- Before field use of water-quality instruments, become familiar with the manufacturer's instructions for calibration, operation, and maintenance.
- The maintenance program must include:
  - Regular cleaning of optical surfaces. Use a lint-free cloth, soft toothbrush, or paintbrush and deionized water for cleaning optical surfaces. Exercise care so as not to damage optical surfaces. Optical surfaces of some instruments may be more easily damaged than others — check manufacturer's recommendations before proceeding with cleaning and use.
  - For deployed, dynamic monitoring, the cleaning frequency should be approximately every 2 to 4 weeks. More frequent cleaning is necessary where biofouling is particularly apparent.
  - Verification that wipers are operational. Change wiper pads when they are excessively dirty or worn; avoid hindering or forcing wiper movement, or scratching optical surfaces.
  - Washing sample cuvettes after each use (wear powderless, disposable laboratory gloves and use a lint-free cloth).
  - Regular calibration or verification against secondary calibration solutions.
  - Examination of collected data for indication of instrument malfunction.
- Test all field instruments in an office or laboratory before use. Record all maintenance and repairs in the instrument logbook.

CALIBRATION 6.7.2

To ensure the collection of reliable turbidity data, carefully follow the standard calibration procedures described below and the instructions from the instrument manufacturer. Even identically calibrated turbidimeters can produce significantly different readings of native-water sources for instruments of different designs. All turbidity instruments are designed to produce equivalent responses to "scratch" formazin (prepared in the office laboratory), the accepted reference solution, despite differences among the designs. The calibration process provides a common point for standardization, and if turbidity were an inherent physical property, then measurements of environmental waters would be expected to have similar numerical values for any instrument. However, the varying particle and color characteristics of environmental waters differ fundamentally from formazin crystals. This has led manufacturers to develop calibration solutions that in some cases are tailored to specific instruments, potentially increasing the magnitude of error if solutions are used improperly. **Where turbidity data are to be compared within or among data-collection projects, the consistent use of sampling, calibration, and measurement equipment and techniques is necessary.**

The USGS follows conventions for turbidity determination established by ASTM International (2003a), which defines three levels of calibration solutions (calibrants): "Reference Turbidity" solutions, "Calibration Turbidity" solutions, and "Calibration Verification" solutions or solids.

- The **Reference Turbidity** solution is a calibrant that a skilled analyst synthesizes reproducibly from traceable raw materials. All other calibrants are traced back to this solution. The reference standard for turbidity is formazin made from scratch (see below for preparation instructions), a polymer with repeating units of $C_2H_4N_2$.
- **Calibration Turbidity** solutions are those that are used to adjust instrument readout, and must be traceable and equivalent to the reference turbidity calibrant to within accepted statistical errors.

TECHNICAL NOTE (4): Acceptable calibration turbidity solutions include dilutions of formazin made from scratch (scratch formazin), commercially prepared stabilized formazin (such as StablCal®, available from Hach Company in formulations of 4,000 turbidity units and lower)[3], and styrene divinylbenzene beads (SDVB) (such as AMCO-AEPA-1® polymer)[3]. Although stabilized formazin calibrants have a much longer shelf life than solutions diluted from scratch formazin, settling of formazin crystals can still be observed when they sit unused. Calibrants made from SDVB have a more uniform grain size than formazin and tend to settle less over time, but often are custom developed for specific instruments and must be purchased accordingly.

- **Calibration Verification** calibrants are those used to perform instrument checks in the field. Calibration verification calibrants may include but are not limited to calibration turbidity solutions. Sealed or solid materials should not be used to adjust instrument performance.

Calibration turbidity solutions and calibration verification calibrants can be instrument specific. Be careful to check the manufacturer's instructions. Use of calibrants with instruments for which they are not designed can introduce significant errors.

All evidence indicates that formazin and stabilized formazin are safe to use as primary turbidity standards when good laboratory practices are followed (Sadar and others, 1998). Standard safety procedures, including wearing laboratory coats, glasses, and gloves, are considered adequate protection for routine use of formazin. The primary hazard from the formazin solution is physical irritation. Of the components in formazin, only formaldehyde will evaporate and

[3]The use of brand names in this report is for example purposes only and does not constitute an endorsement by the U.S. Geological Survey.

cause exposure through the air; however, its concentration in this mixture is well below what is considered to be a health risk. Concentrations in formazin solutions diluted below 4,000 turbidity units will result in exposures that are reduced even further. For more information, see the Material Safety Data Sheet (http://www.ilpi.com/msds/index.html#Internet) or Sadar and others (1998).

TECHNICAL NOTE (5): The raw materials used in the synthesis of scratch formazin do present potential safety concerns. These materials, specifically hydrazine sulfate and hexamethylenetetramine (hexamine), are currently (2004) listed as a suspected carcinogen and an experimental mutagen, respectively. Hydrazine sulfate also is a strong reducing agent and as such requires standard laboratory safety precautions (avoid inhalation, ingestion, and contact with skin, and work in a fume hood). In water, it separates into free hydrazine and sulfuric acid. An excess of hexamethylenetetramine reacts with acid to produce formaldehyde at neutral pH. The formaldehyde then reacts with dissolved hydrazine to produce the formazin polymer. The final product, 4,000 turbidity-unit formazin suspension, contains 3.2 parts per million hydrazine sulfate, 0.1 percent formaldehyde, 0.2 percent formazin, 0.5 percent ammonium sulfate, and 4.7-percent hexamethylenetetramine. Laboratory rats were fed 4,000-NTU formazin at 5,000 mg/kg body weight with no toxic effect (Sadar and others, 1998)

.

Avoid inhalation and ingestion of or skin contact with hydrazine sulfate when preparing formazin solutions. Work in a fume hood.

6.7.2.A CALIBRATION SOLUTION: USE, PREPARATION, AND DILUTION

A stock formazin solution may be prepared in the laboratory or may be purchased from a manufacturer. Serial dilutions are made to achieve the desired calibration interval. **Commercially prepared calibration turbidity solutions are recommended for routine instrument calibration to avoid any safety and quality-assurance concerns.**

Under circumstances in which study personnel need to prepare a stock turbidity suspension, precise laboratory practices are required in order to achieve consistent results.

- Always use turbidity-free water (deionized water passed through a filter media of less than or equal to 0.2 μm) at 20-25ºC for mixing dilutions or suspensions.
- Prepare the stock turbidity suspension monthly and calibrant dilutions immediately prior to instrument calibration. **Calibrant solutions made from diluted scratch formazin are stable for only a few hours to a few days, depending on the concentration** (ASTM, 2003b)**. With the exception of 4,000 NTU formazin, commercial calibration solutions such as StablCal® or AMCO-AEPA-1® must not be diluted because changes will occur in the suspension matrix that will render the dilutions nonlinear.**
- Store reagents, as appropriate, in a dust-free cabinet or refrigerator.

Inconsistent techniques used to dilute calibrants and variable temperatures can add significant measurement error.

To prepare a 4,000 turbidity-unit formazin stock suspension[4]:

1. Wearing laboratory powderless disposable gloves, quantitatively transfer 5.0 g of reagent-grade hydrazine sulfate [$(NH_2)_2 \bullet H_2SO_4$] into approximately 400 mL of turbidity-free water in a 1-L volumetric flask.
2. Quantitatively transfer 50.0 g of reagent-grade hexamethylenetetramine [$(CH_2)_6N_4$] into approximately 400 mL of turbidity-free water in a separate, clean flask; stopper and swirl until the $(CH_2)_6N_4$ is completely dissolved. Filter through a 0.2-µm filter into a clean flask.
3. Quantitatively transfer the filtered hexamethylenetetramine into the flask containing hydrazine sulfate (from step 1). Dilute solution to the 1-L mark with turbidity-free water. Stopper and mix for at least 5 minutes, but no more than 10 minutes.
4. Let stand for 24 hours at 25º ± 1ºC to develop the 4,000 turbidity-unit suspension.
5. Transfer the solution to an opaque, light-blocking, polyethylene bottle and store refrigerated. The 4,000 turbidity-unit stock suspension is stable for about a year, if stored at 20 to 25ºC in amber polyethylene bottles.

To prepare 500 mL of a 400 turbidity-unit calibrant solution, dilute the 4,000 turbidity-unit stock solution by a 1:10 ratio as follows:

1. Mix 50 mL of the 4,000 turbidity-unit stock solution in a 500-mL flask.
2. Dilute to the mark with turbidity-free water and mix.
3. Transfer the solution to an opaque, light blocking, polyethylene bottle and store refrigerated. The 400 turbidity-unit stock solution is stable only for about one day.

[4]Refer to ASTM International (2003a) for detailed instructions.

To prepare a 40 turbidity-unit calibrant solution, dilute the 400 turbidity-unit solution by a 1:10 ratio as follows:

1. Mix 10 mL of the 400 turbidity-unit stock solution in a 100-mL flask.
2. Dilute to the mark with turbidity-free water and mix.
3. Transfer the solution to an opaque, light-blocking, polyethylene bottle. **Prepare the calibrant suspension on the day the calibrant is needed, use it immediately after preparation, and discard unused calibrant. The 40 turbidity-unit stock solution is stable only for about 1 day.**

When chemicals to be used for preparation of reagents are received, mark the dates of receipt and expiration on the container. When a calibrant is prepared, label the container with the contents, date of preparation, expiration date, and preparer's initials. Store formazin in a cool, dark place (a storage cabinet or frost-free refrigerator). After use, pour waste calibration solutions into a labeled glass or plastic container for proper disposal.

Reagents and calibrants must not exceed their shelf life.

6.7.2.B CALIBRATION PROCEDURES

Although calibration principles are similar whether using static or dynamic sensors, in practice the steps taken can be different.

- Benchtop meters use a small, 15- to 25-mL sample holding cell, or "cuvette," which is inserted into the measurement chamber. This results in a static measurement unless additional flowthrough equipment is used.
  - Values must be read from the meter before particle settling can affect the measured turbidity.
  - If particle settling of sand or silt occurs before the measurement can be completed, the sample results must be recorded in the database to reflect the possible bias in the

data. (For input to the USGS NWIS database, the results would be coded with an "E" remark, indicating the value is an "Estimate" only.)

— The cuvettes used for calibrating static turbidimeters are identical to those used in the meter when taking a turbidity reading.

▶ Submersible meters collect data by immersing a turbidity sensor in the sample media, but are calibrated using a separate chamber that allows the sensor to be immersed in the calibrant.

Benchtop (static) turbidimeter calibration

The calibration instructions and procedures that follow are general and should be modified to apply to the instrument being used—check manufacturer's instructions. Refer to table 6.7–5 for a list of supplies commonly used for turbidity measurement.

To calibrate a benchtop turbidimeter:

1. Prepare formazin suspensions as described above.
   - Allow stock solutions to come to room temperature.
   - Calibrate each instrument range using at least two calibrant concentrations, and three or more if the instrument allows it. Use calibrant solutions that bracket the range of the turbidity anticipated in the sample solution.
   - Prepare dilute calibrant fresh from the stock at the time of use—after dilution, the stock suspension is stable only for a few hours.
   - Formazin-based calibrants should be resuspended by inverting the calibrant 25 times (1-second inversion cycle), followed by a 2- to 10-minute wait to allow for bubble removal. Calibrants of 40 turbidity units or less will remain suspended for up to 30 minutes; calibrants greater than 40 turbidity units may require more frequent resuspension.
   - **Do not use calibrants with flocculated suspensions**.
2. Turn on the turbidimeter and allow it to warm up. (Check manufacturer's instructions for equipment startup.)

3. Select the desired turbidity range. Use a calibration range to equal the high value of calibrant for the range of interest.

4. Rinse a clean, dry, scratch-free cell with the highest concentration of the calibrant for the instrument range setting or range of interest. Index-mark the cell to ensure consistent orientation within the instrument. (See manufacturer's instructions for index-marking the cell.)

    a. Hold the sample cell by the rim (top lip), not beneath the lip.
    b. Pour calibrant into the sample cell to the fill mark.
    c. Wipe the exterior of the cell using a soft, lint-free cloth or tissue to remove moisture (condensation) from cell walls.
    d. Apply a thin layer of silicon oil onto the exterior of the cell to reduce condensation on the cell and to mask slight scratches and nicks. Apply silicon oil uniformly onto the blank cell if it will be used on the cell filled with calibrant (follow manufacturer's recommendations).
    e. Before inserting the cell containing calibrant into the instrument, ensure that no air bubbles are present in the cell. If necessary, degas the sample according to manufacturer's instructions. Air bubbles can cause significant positive bias in turbidity measurements (table 6.7-1).

5. Orient the calibration cell in the cell holder according to the index marks—**the calibration cell and sample cell must have identical orientation** when in the instrument-measurement chamber.

6. In the instrument logbook, record the instrument value for each calibrant. Most modern turbidimeters contain calibration curve-fitting capabilities specific to that instrument, allowing the instrument to produce sample readings that may be used directly. If the meter does not have this capability, you will need to construct a calibration curve to correct sample readings to the calibrated turbidity. To determine turbidity using a calibration curve (see American Public Health Association, 2001, for more details on this procedure):

a. Record the instrument response to a range of calibration solutions bracketing the expected turbidity of the sample.
b. Create a graph showing the value of the instrument response (x-axis) against the turbidity value of the calibration solutions (y-axis).
c. Using linear regression, plot a line that encompasses the plotted values.
d. For water samples, input the instrument reading on the x-axis and read the corresponding corrected turbidity value from the y-axis, or determine the corrected y-value from the regression equation on the instrument reading.

7. Adjust the calibration control until the value on the meter equals the value of the calibrant used.

8. Repeat steps 4 through 7 as recommended by the instrument manufacturer for calibration solutions bracketing the range of expected turbidities. Use calibrants representing at least two different turbidities, including the expected maximum and minimum. Ensure that calibrants are within the linear portion of the instrument's operating range.

Submersible (dynamic) turbidity sensor calibration

Most dynamic turbidimeters and multiparameter instruments with turbidity sensors are microprocessor based, with the calibration parameters stored in instrument memory. Turbidity values of the calibrants are user selectable in some instruments, but others have internally established calibration ranges that cannot be changed.

- Check calibrants in the 1 to 5 turbidity-unit (low-level) range to assess the actual performance of the instrument near the detection limit; **instrument reliability often decreases at turbidities less than 2 turbidity units—**consult the manufacturer's specification for the expected accuracy of the measurement.

- Refer to Wagner and others (2000) for instructions on record keeping when cleaning and calibrating continuously deployed instruments, and for acceptable tolerances. Monitor the output carefully to ensure that turbidity readings are stable before confirming the calibration.
- **Calibrate the instrument using calibration turbidity solutions before leaving for the field**. While in the field, check instrument performance periodically using a calibration or verification calibrant and turbidity-free water.
- The optical surface of the sensor must be clean before beginning the calibration procedure. In deployed, continuous monitoring situations, pipes or other structures that house the sensor also may require periodic cleaning.

To calibrate a submersible turbidity sensor *(modify the general instructions that follow as necessary so that they are compatible with the manufacturer's instructions)**:***

1. Prepare a sufficient volume of the selected calibration solution or verification calibrant, as described previously. The volume of calibrant required could be 500 mL for some instruments, particularly if the entire sonde bundle will be immersed.
2. **Select Procedure (A) or (B).** The same procedure, once tested and selected, also should be applied to instruments used in future studies against which the data could be compared.

   Procedure A. Immersion of the entire sonde (bundle of field-measurement sensors, including the turbidity sensor) requires larger volumes of calibrant; calibrant is vulnerable to contamination and dilution. The sonde sensor guard may need to be removed.

   Procedure B. Immersion of turbidity sensor only—depending on sonde configuration, isolation of the turbidity sensor and achieving a bubble-free optical surface could be difficult. This technique minimizes the volume of calibrant required for calibration.
3. Determine the number of calibration points to be used (a minimum of two, but three is preferred) and configure the instrument for this number of points, if applicable.

4. For a zero turbidity-unit calibrant (or turbidity-free water):
   a. Rinse sonde/sensor with deionized water, followed by a portion of the turbidity calibrant.
   b. Immerse sensor in calibrant, or add enough calibrant to cover the sensor in the calibration chamber.
   c. Agitate the sonde/sensor repeatedly to remove bubbles from the optical surface (activate mechanical wiper, if present).
   d. Set sensor vertically on a flat surface or use a ringstand to hold it.
   e. Monitor turbidity readings for 1 to 2 minutes or longer to ensure that readings are stable (consult manufacturer's recommendations and signal-processing information). Record the pre-calibration value in the instrument logbook or on the field sheet.
   f. Confirm the calibration value or adjust the instrument calibration using the manufacturer's instructions.
   g. Remove the sonde/sensor and dry thoroughly to minimize dilution or contamination of the next calibrant.
   h. Discard the calibrant into a labeled waste container and hold for proper disposal.
   i. If measurement of color-derived turbidity is not desired, filter (using a 0.2-µm pore-size filter) an aliquot of the sample water and use the filtered water in place of turbidity-free water.

5. Using a second calibrant with a value near the maximum of the expected turbidity range, repeat steps 4(a-i). Repeat again with a third calibrant near the middle of the expected range if increased accuracy is desired and instrument software permits. If the software does not permit a three-point calibration, the third calibrant can nonetheless be used to document the accuracy of the calibrated instrument near the middle of the expected range. If an "out of range" error is displayed, verify the intended calibrant value and start again with the first (zero) calibrant solution. Repeat the calibration procedure if the measurement is not within the specification. Record all calibration and verification measurements in the instrument logbook.

6. On a one-time basis, determine the maximum value that can be reported by the instrument by holding a lint-free cloth over the optical sensor and recording the turbidity. Use this value as an indicator that turbidity might have been greater than the range of the instrument during measurements in a water body.

Spectrophotometric turbidimeter calibration

Spectrophotometric turbidity measurements, sometimes referred to as absorbtometric or attenuation turbidity, are useful to indicate relative values or to monitor changes in turbidity with time. Spectrophotometers, however, measure light transmission (rather than light scattering) using a narrow, short-wavelength light source, are inaccurate for absolute turbidity measurement, and are unrated for instrument sensitivity. Most of the spectrophotometers used for measuring turbidity are benchtop or portable instruments, so sample handling is similar to that described for benchtop (static) turbidimeters.

- Use spectrophotometry as an indication of optical properties in water only upon careful review of study objectives and alternative available technology.
- Instrument response is negative (that is, the detector response decreases) with increasing turbidity, which is the opposite of traditional turbidity and backscatter instrument responses. Report results in Attenuation Units (AU) or Formazin Attenuation Units (FAU), depending on the light source (table 6.7-4). (The overwhelming majority of available spectrophotometric turbidity instruments use FAU.)

Spectrophotometers commonly have a stored program for turbidity that has been factory calibrated and that can be verified but not adjusted. Check the instrument output against that of a different instrument every few weeks while the instrument is in use. Check the relative accuracy of the turbidity measurement before leaving for the field by inserting calibration turbidity solutions covering the FAU range needed. Accounting for a change in reporting units, calibration steps for spectrophotometric determination are identical to those for static measurement of turbidity, including the possible need for constructing a calibration curve (see instructions under **Benchtop (static) turbidimeter calibration**, steps 1 through 8).

MEASUREMENT 6.7.3

Three methods for field-measurement determinations of turbidity are described in this section: static (or benchtop) determination (6.7.3.A); dynamic (submersible) determination (6.7.3.B); and spectrophotometric (absorptometric) determination (6.7.3.C). Procedures for the use of turbidity instruments are similar for various surface-water and ground-water applications. The sampling methods used and the considerations needed for accurate representation of the intended water conditions, however, depend on the objectives and intended data use of the study and on site type and conditions. Routine sampling of streams by the USGS typically involves isokinetic, depth-integrated sampling methods (NFM 4.1; NFM 6.0.2). Much of the routine sampling of ground water at wells by the USGS involves well purging (NFM 4.2; NFM 6.0.3).

- Before making a turbidity determination, ensure that the instrument to be used has been cleaned and calibrated properly, and that the calibration process has been accurately documented (section 6.7.2).
- Biased or erroneous readings can result from numerous factors, including unmatched cell orientation, colored sample solutions, gas bubbles, condensation, and scratched or dirty sample cells (see tables 6.7–1 and 6.7–2). Condensation on the sample cell commonly occurs when the water sample is much colder than the air temperature.
- **Turbidity measurement is time sensitive and therefore should be completed on-site (preferably in situ)** to avoid effects from (a) biodegradation, growth, settling, or sorption of particulates in the sample; or (b) precipitation of humic acids and minerals (carbonates and hydroxides, for example) caused by changes in sample pH during transport and holding.
- If temporary storage of samples is necessary, collect samples in clean amber bottles, keep out of sunlight, and chill at or below 4°C to prevent biodegradation of solids or biological growth. The holding time must not exceed 24 hours (ASTM International, 2003a).

Turbidities in surface waters can range widely, even within the same water body, depending on local hydrology, sources of sediment or colored materials, and disturbance regimes. Although drinking-water sources often have background turbidities of less than 1 turbidity unit, it is not unusual to measure turbidities of 1,000 or greater, depending on stream and weather conditions (Uhrich and Bragg, 2003). Protocols for determining turbidities in surface waters typically must account for making reliable measurements that span turbidities over one to three orders of magnitude. Use either a dynamic or static method, employing either discharge-weighted, pumped-sample, or grab-sample procedures, as appropriate for site characteristics and study objectives (NFM 6.0). Repeat the measurement three to five times to ensure accuracy and replication within the precision of the instrument.

6.7.3.A STATIC (BENCHTOP) DETERMINATION

The methods described below encompass both white-light nephelometry that meets USEPA specifications for drinking water, and other static methods (for example, ISO 7027) that do not meet USEPA specifications. EPA Method 180.1 is applicable in the range of turbidity from 0 to 40 NTU without dilution, and from about 40 to 1,000 NTU with dilution (U.S. Environmental Protection Agency, 1993). **Note that dilution of environmental samples that contain particulate materials or exhibit other nonlinearity properties can introduce significant errors from subsampling; therefore, dilution is discouraged.** Reporting units will vary with the instrument type used: Consult table 6.7–3 and the turbidity parameter and methods codes spreadsheet (http://water.usgs.gov/owq/turbidity_codes.xls, accessed 9/30/2005). The static method assumes the turbidimeter recently has been calibrated properly with a calibration or verification solution (section 6.7.2).

Benchtop determination of turbidity is especially susceptible to negative bias from particle settling. Visually check for the presence of coarse material (sand or coarse silt) in the sample. Gently agitate the sample, then set it down. **If particles rapidly settle to the bottom (within 3-5 seconds), then coarse materials are present and the sample cannot be measured accurately using the static method.** Static measurements made on such samples therefore must be coded to indicate that accuracy is qualified when being entered into a database. In the USGS NWIS database, for example, the results should be entered with an “E” remark code.

Preliminary steps for benchtop turbidity determination:

1. Warm up the turbidimeter according to the manufacturer's instructions. Put on powderless laboratory gloves.
2. Rinse a clean, dry, scratch-free, index marked cell with a turbidity calibrant within the range of interest.
3. Gently agitate the calibrant, pour the calibrant into the sample cell to the fill mark, and dry the cell exterior with a lint-free cloth.When using a meter recently calibrated with an acceptable calibrant turbidity solution (formazin or styrene-divinylbenzene polymer—see section 6.7.2), a verification calibrant may be used for this check measurement.
4. Follow the manufacturer's instructions for readout of turbidity value and record the turbidity of the calibrant used and the turbidity value measured in the calibration logbook. If readings are not within specifications for the indicated range, recalibrate the instrument for the turbidimeter using accepted calibration turbidity solutions.

Most turbidimeters will correct initial sample readings directly into a final reading based on the stored calibration. If the meter does not have this capability, take the values from a previously constructed calibration curve.

For samples with turbidity less than 40 turbidity units:

1. Measure sample turbidity immediately or as soon as possible upon sample withdrawal.
   a. If discrete subsamples are to be taken from a churn splitter or other sample-compositing device, remove samples for turbidity measurement along with other whole water samples. Avoid pouring the sample into a cuvette from a bottle, if possible. If not possible, then invert the bottle 25 times using a 1-second inversion cycle and pour off the sample immediately to capture suspended particles.

b. For drinking water, use an instrument that complies with EPA Method 180.1 or GLI Method 2. Measurements are reported in NTU or NTRU for EPA 180.1, or in FNMU for GLI Method 2. (See table 6.7–4 to select the appropriate parameter code.)

2. Rinse a freshly cleaned cell with the sample to be tested.
3. For a **discrete (static) sample**, complete the following sequence of steps (through step 4a) without hesitation (skip to step 4 for flowthrough cell measurement).
   a. Gently invert—do not shake—the sample 25 times (ASTM, written commun., undated) to completely disperse the solids, taking care not to entrain air bubbles. Allow air bubbles to disappear before filling the sample cell.
   b. Rapidly pour the sample into a sample cell to the line marked (to the neck if there is no line). Do not touch cell walls with fingers.
   c. Remove condensation from the cell with a clean, soft, lint-free cloth or tissue. If condensation continues, apply a thin coating of silicon oil to the outside of the cell about every third time the cell is wiped dry of moisture. Allow samples to equilibrate to ambient temperature, if necessary, before subsampling to help minimize condensation problems. Note: warming the sample may change particle associations in the water matrix.
   d. Before inserting the sample cell into the meter, ensure that no air bubbles are present in the cell. If necessary, degas the sample according to the manufacturer's instructions. Air bubbles can cause significant positive bias in turbidity measurements (table 6.7–1).
   e. Orient the calibration cell in the cell holder according to the index marks—the calibration cell and sample cell must have identical orientation when in the instrument measurement chamber.

Be sure that sample cells are index marked to indicate orientation. Match orientation so that cells yield the same value when light passes through.

4. Determine the measured turbidity value of the sample directly from the instrument scale or by using the instrument value and calibration curve, as is appropriate for the instrument being used. For samples with less than 1 turbidity unit, see **TECHNICAL NOTE (6)** under step 4d.
   a. Record the very first readings after placement of the sample cell in the measurement chamber. If readings are unstable, then particle settling may be occurring. If so, gently re-invert the cell 25 times and record at least three readings over a short, defined time interval (for example, 30 seconds to 1 minute).
   b. Repeat at least twice with fresh sample, until three or more sample values fall within ±10 percent.
   c. Samples that contain significant color should be diluted if using EPA Method 180.1 (for samples with turbidity greater than 40 units see below *"For samples, including drinking water, with turbidity greater than 40 turbidity units," step 3)*. **Results of diluted samples must be qualified with a "d" in the "Value Qualifier Code" field for data entered into the USGS NWIS database.**
   d. Report the median of the three or more sequential readings that fall within ±10 percent.

> **TECHNICAL NOTE (6):** When using low-level reporting scales, you may need to subtract a correction factor from the reading to correct for stray light. For example, the Hach Company reports the correction for the 0.2-NTU scale to be on the order of 0.04 NTU for the Hach 2100P. The stray-light correction is determined by reading turbidity from an empty instrument (without cuvette).

5. Record the data in reporting units described in table 6.7–4, using the method code that describes the specific instrument in use: Consult table 6.7–3 and the turbidity parameter and methods codes spreadsheet (http://water.usgs.gov/owq/turbidity_codes.xls, accessed 9/30/2005). If particle settling or instability in initial readings was a problem, the results must be qualified as an estimate by using an "E" remark code for data entered into NWIS QWDATA.

For samples, including drinking water, with turbidity greater than 40 turbidity units:

1. Select an appropriate instrument. (See table 6.7–4 to select the appropriate USGS parameter code.)
   - For drinking water, use EPA Method 180.1, a compliant instrument, and NTU or NTRU reporting units; alternatively, select the GLI Method 2, a compliant instrument, and FNMU reporting units. Reporting units for these methods must be remarked with an "E" code in NWIS for turbidities greater than 40.
   - For study objectives other than drinking water, choose instruments according to information provided in figure 6.7–2 and table 6.7–3.
2. Obtain a discrete sample.
   - For drinking-water samples, proceed to step 3.
   - For non-drinking-water samples, skip to step 4.
3. For drinking-water samples, dilution is required to comply with USEPA regulations.
   a. Dilute the sample with one or more equal volumes of turbidity-free water until turbidity is less than 40 turbidity units after mixing and degassing.
   b. Record the volume of turbidity-free water used for dilution. Follow steps 1-5 from the previous section for samples with turbidity less than 40 turbidity units.
   c. Skip to step 5, below
4. For non-drinking-water samples (where USEPA compliance is not required), with 100 and 1,000 turbidity-unit ranges only — place a cell riser (if available) into the cell holder before inserting the sample cell. This decreases the length of the light path in order to improve the linearity of measurements. **Do not use the cell riser for the lower turbidity ranges.**
   a. For turbidimeters with adjustable ranges and signal-processing capabilities (for instance, ratio mode to compensate for high particle densities), select the desired configuration (table 6.7–3) and operate according to manufacturer's recommendations. Some instruments will automatically switch to different modes (for example, ratio mode) or to a different light source. Record instrument mode on field sheets.
   b. Select the desired range on the turbidimeter.

Dilutions can introduce errors if coarse material is present or if the sample matrix changes with the addition of diluant. When making dilutions, perform at least three at approximately 80, 50, and 20 percent of the original concentration. Record the turbidity of each dilution and determine if they are linear and correlate positively with the percentage diluted. If the response is nonlinear, alternative instrument designs that better compensate for interferences should be considered. Do not forget to adjust the turbidity value of diluted samples using the dilution factor.

5. Fill the cell with sample water:
   a. Hold the cell by the rim (top lip), not beneath the lip.
   b. Gently agitate the sample 25 times. Without hesitation, carefully but rapidly pour sample water into the cell to the fill mark.
   c. Wipe the exterior of the cell using a soft, lint-free cloth or tissue to remove moisture (condensation) from cell walls.
   d. If necessary, apply a thin layer of silicon oil (table 6.7–1) onto the exterior of the cell to reduce condensation on the cell and mask slight scratches and nicks.
   e. If rapid particle settling is occurring, steadily invert the cell 25 times, taking care not to shake too vigorously, which could entrain gases in the sample.

6. Record the sample turbidity.

Most modern turbidimeters will adjust initial sample readings directly into a final reading based on the previous calibration. If the meter does not have this capability, you will need to read values from a calibration curve constructed previously. See step 6 under "Benchtop (static) turbidimeter calibration" for instructions on constructing and using calibration curves.

a. Record the very first readings after placement of the sample cell in the measurement chamber. If readings are unstable, particle settling may be occurring: gently re-invert the cell 25 times and record at least three readings over a defined time interval (for example, 30 seconds to 1 minute).
b. Repeat at least twice with fresh sample until three or more sample values fall within ±10 percent.
c. Samples that contain significant color should be diluted if using EPA Method 180.1. **Results of diluted samples must be qualified with a "d" in the "Value Qualifier Code" field for data entered into the USGS NWIS database.**
d. Report the median of the three or more sequential readings that fall within ±10 percent.

For diluted water samples, the measured turbidity must be converted based on the amount of dilution, according to the following equation:

$$T_s = T_d \times \frac{(V_o + V_s)}{V_s},$$

where T_s= turbidity of the environmental sample, T_d=turbidity of the diluted sample, V_o = volume of turbidity-free water in the diluted mixture, and V_s= volume of the environmental sample in the diluted mixture.

EXAMPLE: If five volumes of turbidity-free water were added to one volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample is computed as 180 units.

e. Report turbidity as follows, using method codes as described in http://water.usgs.gov/owq/turbidity_codes.xls (accessed 9/30/2005)[5]:
   - For EPA Method 180.1, use NTU or NTRU.
   - For GLI Method 2, use FNMU.
   - For non-diluted, non-USEPA-compliant measurements, use the reporting units described in table 6.7–4.

In contrast to surface waters, natural turbidity in ground water generally is less than 5 turbidity units. Natural ground-water turbidity of up to 19 turbidity units has been reported for some environmental settings (Nightingale and Bianchi, 1977; Strausberg, 1983; Puls and Powell, 1992). Contaminated ground-water systems, however, can have considerably higher turbidity (Wells and others, 1989; Gschwend and others, 1990; Puls and Powell, 1992; Backhus and others, 1993). Measuring turbidity in ground water requires special considerations and procedures. For effervescent ground water, a degassing apparatus may be required; follow manufacturer's instructions.

- **During well development—**Monitor turbidity caused by well installation, recording consecutive measurements to document decreases in turbidity as development proceeds.
- **During well purging—**Monitor changes in turbidity by taking sequential readings until purging criteria are met (NFM 6.0). The final stabilized turbidity value should be equal to or less than the value recorded at the end of well development. A decrease in turbidity values during purging can indicate mitigation of subsurface disturbance caused by well installation and by deployment of data-collection equipment in the well.
- **For dynamic measurement—**Report the median of the three or more sequential measurements that meet the ±10-percent criterion for stability (NFM 6.0).
- **For discrete-sample measurement using a turbidimeter or spectrophotometer:**
  - **Bailers are not recommended** for collecting turbidity samples, as bailer deployment can increase turbidity.
  - Do not collect the discharge passing through the flowthrough chamber in which pH, conductivity, or other field-measurement sensors are installed.

[5]Diluted samples must be qualified with a "d" in the "Value Qualifier Code" field when entering data into NWIS.

— **Pump the ground-water sample** directly from the sample discharge line into a precleaned glass or polyethylene sample-collection bottle.

— Subsample into a cuvette and measure turbidity according to instructions for static determination (steps 3 through 5 above).

Multiparameter instruments can be used with a flowthrough chamber (instead of being deployed in situ) for monitoring ground-water field measurements. See the section below on dynamic determination of turbidity.

6.7.3.B DYNAMIC (SUBMERSIBLE-SENSOR) DETERMINATION

Determination of turbidity using a submersible sensor or sensor in a multiparameter sonde is useful for site-specific water-quality studies. Such turbidity data can be used for watershed investigations; for example, for determination of visual impairment (Davies-Colley and Smith, 2001), for correlation with concentrations of suspended sediment, total phosphorus, or other chemical constituents, and indicator bacteria (Christensen and others, 2000; Uhrich and Bragg, 2003), and for long-term monitoring. Turbidity sensors for these applications utilize a variety of different light sources and other options to compensate for interferences (fig. 6.7–2, table 6.7–3).

Multiparameter instruments with internal batteries and memory can be used in surface-water studies that require long-term deployment. Guidelines for long-term instrument deployment fall under the topic of continuous monitors, and are beyond the scope of this section—refer to the manufacturer's instructions and recommendations, and to guidance documents such as Wagner and others (2000).

Some submersible turbidity sensors can be adjusted to operate within differing turbidity ranges. For example, although the maximum turbidity based on factory settings is just over 1,000 FNU, the YSI 6026 can be factory adjusted to read turbidities up to 4,000 FNU, allowing readings to be obtained that would otherwise be off scale. The adjustment, however, is specific to the individual instrument, with calibration being non-linear between 1,000 and 4,000 FNU; hence,

readings in this high range are not reproducible between instruments (M. Lizotte, YSI Environmental, written commun., May 2003). Any such adjustments made to an instrument's operating range must be documented in the instrument's logbook and in applicable field notes.

Dynamic determination generally reflects the dynamic conditions in a water body more accurately than static measurements of discrete samples because it avoids problems of particle settling. Instrumentation of this type, however, is not approved by the USEPA for evaluating drinking water.

The following procedures apply to in situ determination and to determination of turbidity in a flowthrough chamber:

1. Calibrate the instrument in the laboratory or office using a calibration solution before leaving for the field (see section 6.7.2).
2. At the field site, verify that the instrument has retained its calibration within 5 percent. If it fails verification, then the instrument must be recalibrated.
3. Follow procedures for selection of surface-water and ground-water sampling locations and for dynamic (**Procedure A**) or flowthrough-chamber (**Procedure B**) field measurements, as described in NFM 6.0.

   Procedure A: Dynamic measurement—Immerse the multi-parameter sonde or single turbidity sensor in the water body.

   Procedure B: Flowthrough chamber (ground water only)—Secure chamber cover over sonde/sensor to form an air-tight and water-tight seal. Discharge the first sample aliquot to waste, then open the connection to the flowthrough chamber and pump a sample from the water source to the flowthrough chamber according to instructions in NFM 6.0.3.

4. Activate the instrument to display turbidity values in real time.
5. Agitate the turbidity sensor to remove bubbles from the optical surface: move the sensor up and down or in a circular pattern and (or) activate the wiper mechanism, if available.
6. Monitor turbidity readings as described for other field measurements in NFM 6.0.
    - Allow at least 2 minutes before recording the required number of sequential readings. Some instruments may require as much as 10-20 minutes warmup time.
    - Stability is reached if values for three (for in situ procedure) to five (for flowthrough-chamber procedure) or more sequential readings, spaced at regular time increments, are within 10 percent.
7. Record turbidity readings on the field form and in field notes, including the instrument manufacturer and model. Use reporting units appropriate for the instrument, as described in tables 6.7–3 and 6.7–4.
8. **Surface-water sites—**Repeat steps 5–7 for dynamic measurements (**Procedure A**) at each vertical to be measured. Determine the number of vertical locations; refer to NFM 6.0.2.A and NFM 4.1.
9. Before leaving the field, clean the sonde/sensor with a thorough rinse of deionized water and place it in the storage vessel. Most instruments require a small amount of deionized water to be stored in the storage vessel with the sensors. **Follow the manufacturer's recommendations for storage of sondes/sensors.**
10. Record data in the database in reporting units as described in table 6.7–4, using method codes specific to the instrument in use (http://water.usgs.gov/owq/turbidity_codes.xls, accessed 9/30/2005).
11. If turbidities are higher than the instrument range, dilutions will be necessary. Turbidity will need to be measured with static methods. Take a representative sample and dilute it with one or more equal volumes of turbidity-free water, recording the volume of water used for dilution. In such cases, **qualify the resulting data with a "d" in the "Value Qualifier Code" field in NWIS**.
12. **Quality control.** Periodically check instrument performance by placing a primary or secondary calibration solution in the instrument storage vessel and comparing the standard value with the reading displayed. Record in the instrument maintenance logbook all the readings obtained.

SPECTROPHOTOMETRIC DETERMINATION 6.7.3.C

The attenuation method described below uses a field spectrophotometer to provide a relative measure of the sample turbidity. The spectrophotometer directs a beam of light through the sample at a specific wavelength and measures the amount of transmitted light reaching the "transmitted" detector (fig. 6.7–1). The decrease in the detected light intensity caused by absorption or scattering in the sample is calibrated to accepted calibration turbidity solutions (see 6.7.1.C). Spectrophotometric measurement of turbidity yields readings in AU or FAU, depending on the light source.

- **This method is not approved by the USEPA** and is subject to many interferences. It is a useful method, for example, if the purpose for the turbidity determination is as an indicator of ambient or "stabilized" conditions during well development or purging.
- **Turbidity values less than 50 FAU—the range for most surface water and ground water—are inaccurate using this method** and the procedure is recommended only as a measure of relative turbidity among different samples.

.

An FAU is equivalent to an NTU when measuring formazin, but they are not necessarily equivalent when measuring water samples or other types of standards. Relations among different instrument types are site specific. Be careful to enter absorption-derived turbidity values into the data base using the appropriate reporting units, parameter codes, and method codes according to tables 6.7–3 and the methods and parameter codes spreadsheet (http://water.usgs.gov/owq/turbidity_codes.xls).

To make spectrophotometric determinations of turbidity:

1. Before starting, check operating instructions for the specific instrument in use**.**
2. Enter the stored program number for turbidity, if any. Record the light wavelength used. A wavelength of 860 nm (bandwidth 60 nm) is specified by ISO 7027 for reporting in FAU.
3. Use a set of clean, matched 10-mL sample cells.
4. Calibrate according to instructions in the instrument's operating manual (see section 6.7.2).
5. If recently calibrated, take check measurements using calibration solutions that bracket the range anticipated in the sample solution. **Clean the 10-mL cell after using calibrants.**
6. Fill one cell to the 10-mL mark with turbidity-free water and cap with a stopper. NOTE: If measurement of color-derived turbidity is not desired, filter (using a 0.2-µm pore-size filter) an aliquot of the sample water and use this water in place of turbidity-free water.
7. Place blank sample into the cell holder, close the light shield, and verify a zero reading.
8. Fill the other cell to the 10-mL mark with sample water and cap with a stopper. Gently invert 25 times to suspend all particulates.
9. Carefully place sample into the cell holder and close the light shield. Record this reading in AU or FAU.

QUALITY-ASSURANCE PROCEDURES 6.7.4

Quality-assurance procedures should be developed in accordance with the objectives of the sampling or monitoring plan. The primary emphasis should be on quantifying the sources of variability and bias in turbidity measurements that can affect the utility of the data being collected. **Where turbidity from one water source will be compared with turbidity from another source or against a numerical criterion, the use of consistent procedures, instrumentation, and supplies is critical.**

VARIABILITY 6.7.4.A

Sources of variability include the different instruments in use (even similar models), differing subsampling techniques, different operators, spatial and temporal variations in the water body being measured, and different sampling procedures being used. The data resulting from static turbidity determinations also can be negatively biased from particle settling.

Variability in turbidity can be quantified through repeated measurements of turbidity at different times, using different instrumentation, or using different methods. In some cases it might be useful to compare results of a field-turbidity measurement with that of a laboratory-analyzed sample. Keep in mind, however, that sample properties that affect turbidity can degrade during sample transit and storage (see section 6.7.3). The following are examples of tests that can be performed periodically for quality control of some sources of variability in turbidity determinations.

- **Static determination**
  - **Measurement variability:** For one cuvette with sample and gently agitate to keep particulates in suspension. Measure the turbidity and remove the cuvette from the turbidimeter. Repeat at least three times, using the same cuvette. Record each reading and determine the standard deviation of the measurements. Consider submitting replicate samples for laboratory analysis. These procedures may not adequately characterize measurement variability that is caused by particle settling.

- **Subsampling variability:** For one water sample, agitate the sample, then withdraw an aliquot into the cuvette, measure turbidity, discard the sample, and clean the cuvette. Repeat at least three times. Record each reading and determine the standard deviation of the measurements.
- **Operator variability:** Split one water sample into two or more subsamples using a churn splitter. Have different operators prepare cuvettes and measure turbidity on the subsamples. Consider submitting samples for laboratory analysis.
- **Sampling variability:** Collect at least two independent samples from the source using standard techniques. Prepare turbidity cuvettes for each sample and measure turbidity.

▶ **Dynamic Determination**

- **Cross-sectional variability:** At a field site, measure turbidity at a number of verticals across the stream width (see NFM 4 and 6.0). Compare against measurements at the centroid, stream margins, locations for continuous monitors, different depths, or against a static measurement from a composite sample using a meter that is optically compatible with the dynamic meter. Keep in mind that the static measurement will likely be biased low if sand or coarse silt are present.
- **Measurement variability:** At a field site, repeat turbidity measurements three or more times at the same location, one after another. Record these values after removing the meter from the water. Use the same instrument for each set of measurements. Consider submitting samples for laboratory analysis.
- **Operator variability:** At a field site, have two or more people determine turbidity at the established measurement location. Use the same instrument for each set of measurements, although it can be calibrated by each person independently to incorporate all sources of variability.

If sand or coarse silt are present in the sample, qualify your static-determination data being entered into NWIS with an "E" remark code.

BIAS 6.7.4.B

Sources of bias can include effects on measurements from various properties of water (table 6.7–1), interferences (table 6.7–2), sampling and subsampling techniques, instrument drift, biofouling, sensor damage, different operators, and different protocols being employed. Bias in turbidity is quantified through measurements of turbidity against known calibration solutions, at different times, using different instrumentation, or with different methods. This is particularly important before and after a measurement series, either in a laboratory or when servicing a continuous monitor in the field. Following are examples of quality-assurance tests that can be performed periodically for static or dynamic determinations of turbidity.

- **Instrument Drift**: After a series of measurements and prior to calibration, measure turbidity using known calibrants, including turbidity-free water or zero-turbidity calibration solution and a calibration (or "check") solution near the maximum calibrated range. Record the turbidity before making any adjustments to instrument calibration. Bias is computed as the percent difference between readings before calibration and readings at the same range after calibration. Instrument drift is most important to document in continuous monitoring applications.
- **Fouling**: After a series of measurements and before calibration, measure source-water turbidity using known calibrants, including turbidity-free water or zero-turbidity calibration solution and a calibration (or "check") solution near the maximum calibrated range. Record data. Clean the cuvette or submersible sensor and repeat measurements of source water and calibrants. Record data. Calculate bias as the percent difference between the calibrant reading of the uncleaned sensor and the cleaned sensor.
- **Operator Bias:** Similar to Operator Variability (above), bias can result from inconsistencies in methods among different operators. Split one water sample into two or more subsamples using a churn splitter. Have different operators prepare cuvettes and measure turbidity on the subsamples. Consider submitting samples to a laboratory for analysis. Calculate bias as the percent difference between the turbidity readings obtained by the different operators.

6.7.5 DATA REPORTING AND INTERPRETATION

To minimize comparison of data derived from substantially different instrument designs, USGS turbidity data are stored according to the instrument designs and reporting units indicated in table 6.7–4, with the method codes describing the specific instrument used. **Parameter codes associated with instrument design and reporting units, and method codes associated with individual instruments are detailed in the Excel spreadsheet at http://water.usgs.gov/owq/turbidity_codes.xls (accessed 9/30/2005).** Method codes are used with these data to provide information that can be used to understand potential differences in turbidity data.

In some cases, instruments are designed to operate in different modes (for example ratiometric or non-ratiometric). Such instruments are listed multiple times in the spreadsheet at http://water.usgs.gov/owq/turbidity_codes.xls (accessed 9/30/2005), corresponding to different parameter codes to distinguish their different settings. Be careful to document all instrument settings and dilution factors, and use parameter codes and method codes appropriate for instrument settings. For data storage in NWIS, samples with noticeable sand or coarse materials that were measured by static techniques must be qualified as Estimates with an "E" in the Remark code, and diluted samples must be entered with a "d" in the Value Qualifier Code field.

- USGS personnel: Do not use parameter codes P00076 and P61028. These codes are reserved for historical turbidity data for which an equipment method cannot be assigned.

Guidelines for reporting turbidity measurements to the nearest acceptable digit according to EPA Method 180.1, GLI Method 2, ASTM, and ISO 7027 methods are listed in table 6.7–6. The indicated values represent the least significant digit in the measurement. Reported turbidity values should be rounded to this level of precision. For example, a value of 43.12 units displayed by an instrument would be reported as 45 under USEPA guidelines, but as 43 under ASTM guidelines. In contrast, a value of 13.42 units displayed by an instrument would be reported as 13 under all the guidelines. For most applications, the USGS will conform to ASTM guidelines unless data were specifically collected for drinking-water compliance (using either EPA Method 180.1, GLI Method 2, or ISO 7027).

Traditionally, the USGS has censored data below 2 NTU as not-detected (less than 2). However, improvements in instrument capabilities have resulted in greater reliability at this low end. Based on input from instrument manufacturers, ASTM has chosen to report data below 1 to the nearest 0.05 unit, and to the nearest 0.1 for data ranging between 1 and 10. Because turbidities in this range should be free of appreciable color or settleable materials, static methods should provide reasonable comparisons with dynamic methods. Before publishing such data, study personnel should consider submitting samples of low-turbidity water to the NWQL or other laboratory for confirmation of low-end resolution and reproducibility.

Additionally, the high end of an instrument's range should be determined. Data greater than this value should be censored as greater than the maximum value. For dynamic sensors on a submersible sonde, cover the optics with a piece of lint-free cloth and record the resulting turbidity. Confirm this value with the manufacturer's recommendations. Qualify data having the maximum value by showing a ">" remark code in NWIS.

Table 6.7–6. Guidelines for reporting turbidity units

[For ASTM and USGS measurements, refer to table 6.7—3 for reporting units based on instrument design. **Abbreviations:** USGS, U.S. Geological Survey; ASTM, ASTM International; EPA 180.1, U.S. Environmental Protection Agency method 180.1 (1993); GLI, Great Lakes Instruments; ISO 7027, International Organization for Standardization method 7027 (1999); NTU, nephelometric turbidity units; FNMU, Formazin Nephelometric Multibeam Units; FNU, Formazin Nephelometric Units; N/A, not applicable;<, less than; ≥, equal to or greater than]

Turbidity Reading	USGS	ASTM	EPA 180.1 (NTU)	GLI Method 2 (FNMU)	ISO 7027 (FNU)
0—<1	0.05	0.05	0.05	0.05	0.01
1—<10	.1	.1	.1	.1	.1
10—<40	1	1	1	1	1
40—<100	1	1	5	5	N/A
100—<400	10	10	10	10	N/A
400–<1,000	10	10	50	50	N/A
≥1,000	50	50	100	100	N/A

6.7.6 TROUBLESHOOTING

Consult the instrument manufacturer for additional guidance if the suggestions shown on table 6.7–7 do not remedy the problem encountered.

Table 6.7–7. Troubleshooting guide for field turbidity measurement

Symptom	Possible cause and corrective action
Erratic reading	• Check voltage of the batteries: replace weak batteries with new batteries. • Condensation on cell wall of static turbidimeter: see "Moisture" symptom. • Bubbles in sampling system or on optical surface of sensor: tap sample line to flowthrough cell or chamber systems to dislodge bubbles; adjust degassing apparatus; remove bubbles on sonde/sensor system by agitating the unit repeatedly or by activating the wiper mechanism.
Unusually high or low turbidity	• Bubbles in sampling system or on optical surface of sensor: see "Erratic reading" symptom. • Fouling of optical surfaces. Clean with lint-free cloth or toothbrush. • Wiper mechanism is "parking" on optical surfaces. Use software to reset wiper, or replace wiper mechanism (may require factory repair). • Inappropriate turbidimeter for environmental conditions. See tables 6.7–1, 6.7–2, and 6.7–3, or figure 6.7–2 to determine most appropriate turbidimeter type.
Calibration value "out of range"	• Contaminated calibrant solution or value entered incorrectly. Verify intended calibrant value and start over. If problem persists, try using a different batch of calibrant solution.
Readings first appear stable, then begin to increase inexplicably	• Check for moisture on cell wall: see "Moisture" symptom.
Moisture condensation on cell wall (static turbidimeter or spectrophotometer)	• Wipe cell dry with soft, lint-free cloth. • Apply a thin veneer of silicon oil (first check instrument manufacturer's instructions). • Add gas sweep to system.
Blank samples or reference material standards do not read accurately	• Check that the cells are oriented as instructed. • Check age/expiration of calibrant solutions. • Check accuracy against that of another instrument.

SELECTED REFERENCES

American Public Health Association, 2001, 2130 B. Turbidity, *in* Clesceri, L.S., and others, ed., Standard Methods for the Examination of Water and Wastewater, 20th Edition: Washington, D.C., American Public Health Association, p. 3.

ASTM International, 2003a, D1889–00 Standard test method for turbidity of water, *in* ASTM International, Annual Book of ASTM Standards, Water and Environmental Technology, 2003, v. 11.01, West Conshohocken, Pennsylvania, 6 p.

ASTM International, 2003b, D6855–03 Standard test method for determination of turbidity below 5 NTU in static mode: ASTM International, Annual Book of Standards, Water and Environmental Technology, v. 11.01, West Conshohocken, Pennsylvania.

Backhus, D.A., Ryan, J.N., Groher, D.M., MacFarlane, J.K., and Gschwend, P.M., 1993, Sampling colloids and colloid-associated contaminants in ground water: Ground Water, v. 31, no. 3, p. 466–479.

Christensen, V.G., Jian, X., and Ziegler, A.C., 2000, Regression analysis and real-time water-quality monitoring to estimate constituent concentrations, loads, and yields in the Little Arkansas River, south-central Kansas, 1995–99: U.S. Geological Survey Water-Resources Investigations Report 00–4126, 36 p., accessed March 25, 2004, at http://ks.water.usgs.gov/Kansas/pubs/reports/wrir.00–4126.html.

Davies-Colley, R.J., and Smith, D.G., 2001, Turbidity, suspended sediment, and water clarity—A review: Journal of the American Water Resources Association, v. 37, no. 5, p. 1085–1101.

Gray, J.R., and Glysson, G.D., 2003, Proceedings of the federal interagency workshop on turbidity and other sediment surrogates, April 30-May 2, 2002, Reno, Nevada: U.S. Geological Survey Circular 1250, 56 p., accessed March 25, 2004, at http://water.usgs.gov/pubs/circ/2003/circ1250/.

Great Lakes Instrument Company, undated, Technical Bulletin Number T1-Turbidity Measurement, Rev 2–193: Loveland, CO.

Gschwend, P.M., Backhus, D.A., MacFarlane, J.K., and Page, A.L., 1990, Mobilization of colloids in groundwater due to infiltration of water at a coal ash disposal site: Journal of Contaminant Hydrology, v. 6, p. 307-320.

International Organization for Standardization, 1999, Water quality — determination of turbidity: Geneva, Switzerland, International Organization for Standardization, ISO 7027, 10 p.

Nightingale, H.I., and Bianchi, W.C., 1977, Ground-water turbidity resulting from artificial recharge: Ground Water, v. 15, no. 2, p. 146-152.

Puls, R.W., and Powell, R.M., 1992, Acquisition of representative ground water quality samples for metals: Ground Water Monitoring Review, v. 12, no. 3, p. 167-176.

Sadar, M.J., 1998, Turbidity science: Loveland, CO, Hach Company, Technical Information Series—Booklet No. 11, 26 p., accessed March 25, 2004, at http://www.hach.com/fmmimghach?/CODE:L7061549|1.

Sadar, M., Foster, A., Gustafson, D., and Schlegel, J., 1998, Safety of formazin and StablCal™ stabilized formazin as primary turbidity standards: Loveland, Co, Hach Company, Technical Notes, 10 p., accessed May 21, 2003, at http://www.hach.com/fmmimghach?/CODE:L14561511|1

Strausberg, S.I., 1983, Turbidity interferes with accuracy in heavy metal concentrations: Industrial Wastes, v. 29, no. 2, p. 16-21.

Sutherland, T.F., Lane, P.M., Amos, C.L., Downing, J., 2000, The calibration of optical backscatter sensors for suspended sediment of varying darkness levels: Marine Geology, v. 162, p. 587-597.

Uhrich, M.A., and Bragg, H.M., 2003, Monitoring instream turbidity to estimate continuous suspended-sediment loads and yields and clay-water volumes in the upper North Santiam River Basin, Oregon, 1998-2000: U.S. Geological Survey Water-Resources Investigations Report 03–4098, 43 p.

U.S. Environmental Protection Agency, 1993, Methods for the determination of inorganic substances in environmental samples: Cincinatti, Ohio, U.S. Environmental Protection Agency EPA/600/R–93/100, 178 p.

U.S. Environmental Protection Agency, 1999, Guidance manual for compliance with the Interim Enhanced Surface Water Treatment Rule—Turbidity provisions: Washington, D.C., U. S. Environmental Protection Agency, Office of Water, EPA 815-R-99-010, variously paged.

U.S. Environmental Protection Agency, 2002a, Federal Water Pollution Control Act (as amended through P.L. 107-3-3, Nov. 27, 2002), 33 U.S.C 1251 et. seq., accessed March 25, 2004, at http://www.epa.gov/region5/water/cwa.htm.

U.S. Environmental Protection Agency, 2002b, Federal Register, Volume 67, No. 209, Section III, October 29, 2002, p. 65888–65902.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, available online at http://pubs.water.usgs.gov/twri9A.

Wagner, R.J., Mattraw, H.C., Ritz, G.F., and Smith, B.A., 2000*, Guidelines and standard procedures for continuous water-quality monitors—Site selection, field operation, calibration, record computation, and reporting: U. S. Geological Survey Water-Resources Investigations Report 00–4252, 53 p., accessed March 25, 2004, at http://water.usgs.gov/pubs/wri/wri004252/.

Wells, M.C., Magaritz, Mordeckai, Ameil, A.J., Rophe, Benjamin, and Ronen, Daniel, 1989, Determination of in situ metal partitioning between particulate matter and ground water: Naturwissenchaften, v. 76, no. 12, p. 568-570.

Wilde, F.D., and Radtke, D.B., August 2005, General information and guidelines (ver. 1.2): U. S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, section 6.0, accessed September 19, 2005, at http://water.usgs.gov/owq/FieldManual/Chapter6/6.0_contents.html.

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., September 1999, Collection of water samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed Sept. 22, 2005 at http://pubs.water.usgs.gov/twri9A4/.

* The revised version of this report was "in press" at the time of this writing and is intended to replace Wagner and others (2000) upon publication. The revised report will be referenced as Wagner, R.J., Boulger, R.W., and Smith, B.A., 2005, Revised guidelines and standard procedures for continuous water-quality monitors: Station operation, record computation, and data reporting: U.S. Geological Survey Techniques and Methods, book 9, chap. B.

TEMPERATURE 6.1

Revised by **Franceska D. Wilde**

Page left blank intentionally.

TEMPERATURE 6.1

Measurements of air and water temperature at a field site are essential for water-quality data collection. Determination of dissolved-oxygen concentrations, conductivity, pH, rate and equilibria of chemical reactions, biological activity, and fluid properties relies on accurate temperature measurements.

Accurate air- and water-temperature data are essential to document thermal alterations to the environment caused by natural phenomena and by human activities. Water temperature can be subject to environmental regulation and monitoring by State and local agencies.

TEMPERATURE: a measure of warmth or coldness of a substance with reference to a standard value.

This section describes methods for measuring temperature in air, surface water, and ground water. The methods are appropriate for fresh to saline waters.

- A thermometer is any device used to measure temperature, consisting of a temperature sensor and some type of calibrated scale or readout device. Liquid-in-glass thermometers and thermistor thermometers are commonly used to measure air and water temperature.[1]
- The U.S. Geological Survey (USGS) uses the Centigrade or Celsius (C) scale for measuring temperature.

[1]Some of the equipment and procedures recommended herein may not reflect the most recent technological advances; in this case, follow the manufacturer's instructions but comply with standard USGS quality-control practices.

6.1.1 EQUIPMENT AND SUPPLIES

Thermometers and other temperature-measurement equipment and supplies must be tested before each field trip and cleaned soon after use (table 6.1–1). Each temperature instrument must have a log book in which all calibrations and repairs are recorded, along with the manufacturer make and model and serial or property number.

Table 6.1–1. Equipment and supplies used for measuring temperature[1]
[–, minus; +, plus; °C, degrees Celsius; L, liter; µS/cm, microsiemens per centimeter at 25°C]

- ✓ Calibration thermometer, liquid-in-glass or electronic-thermistor thermometer, either National Institute of Standards and Technology (NIST) certified or manufacturer-certified as NIST traceable. Must carry certificate of NIST traceability; its use not allowed after expiration of certification.
  - Temperature range, at least –5 to +45°C
  - 0.1°C graduations (liquid-in-glass) or less
- ✓ Thermometer, liquid-in-glass sensor, nonmercury-filled for field use
  - Temperature range, at least –5 to +45°C
  - Minimum 0.5°C graduated
  - Calibrated accuracy within 1 percent of full scale or 0.5°C, whichever is less
  - Calibrated and office-laboratory certified against a properly certified calibration thermometer (see above)
- ✓ Thermistor Thermometer
  - Calibrated accuracy within 0.1°C to 0.2°C
  - Digital readout to at least 0.1°C
  - Office-laboratory certified against a calibration thermometer (see above)
- ✓ Dewar flask and (or) plastic beakers (assorted sizes)
- ✓ Water bath, refrigerated (if available—see section 6.1.2)
- ✓ Soap solution (1 L), nonphosphate laboratory detergent
- ✓ Deionized water (1 L), maximum conductivity of 1 µS/cm
- ✓ Flowthrough chamber (for ground-water applications as an alternative to instruments with downhole capabilities)
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Log book, for recording all calibrations, maintenance, and repairs

[1]Modify this list to meet specific needs of the field effort.

Temperature-measuring instruments for field and laboratory (calibration) use can be either a liquid-in-glass or thermistor thermometer. Field personnel should be familiar with the instructions for use of the thermometer that are provided by the manufacturer.

- **Liquid-in-glass field thermometer**—Total immersion thermometers that are filled with a stable liquid, such as alcohol, are recommended for water measurements in the field. (Partial immersion thermometers are not recommended: these have a ring or other mark to indicate the required immersion depth.) Thermometers for field use must not be mercury filled. Before making temperature measurements, check the type of liquid-filled thermometer being used.
- **Thermistor thermometer**—A thermistor thermometer is an electrical device made of a solid semiconductor with a large temperature coefficient of resistivity. An electrical signal processor (meter) converts changes in resistance to a readout calibrated in temperature units. Thermistors are incorporated into digital thermometers, individual-parameter instruments (such as conductivity and pH meters), and multiparameter instruments used for surface-water and ground-water measurements.

CAUTION:
Do not use mercury-filled thermometers in the field.

MAINTENANCE, CLEANING, AND STORAGE

Liquid-in-glass and thermistor thermometers can become damaged or out of calibration, especially as a consequence of thermal shock or extended exposure to direct sunlight. It is important to be familiar with and to follow the manufacturer's instructions for use and care.

- Keep a log book for each thermometer in which the date, time, and location of every calibration are recorded.
  - — Avoid direct exposure of the thermometer to sunlight.
  - — Avoid submerging the thermometer sensor in corrosive solutions.
  - — Follow the calibration guidelines and protocols described in section 6.1.2.

- — Digital thermometer casings should not be submerged in water unless the manufacturer affirms that they are waterproof. Do not allow any liquid to enter open jacks that are part of some digital thermometers.

- Keep thermometers clean.
  - — Clean thermometer sensors with a soft cloth dipped in a mild solution of lukewarm water and nonphosphate detergent.
  - — If the digital thermometer case needs to be disinfected, use a weak (0.005 percent) bleach solution.
  - — **Do not autoclave the thermometer** (unless autoclaving is sanctioned by the manufacturer).
  - — If your digital thermometer has a detachable sensor with a plug termination, periodically wipe off or clean the sensor contacts. **Dirty contacts can affect temperature readings.**
  - — Blot the thermometer sensor dry after use.
  - — To clean an LCD lens, use only plastic-approved lens cleaners; do not use alcohol, acetone, or other harsh chemicals, as these will fog the lens.

- Store thermometers securely when not in use.
  - — Keep thermometers in a clean protective case when not in use. Each thermometer sensor and the case must be free of sand and debris.
  - — Keep thermometers dry and in a protective case during transit.
  - — Store liquid-filled thermometers with the bulb down.
  - — Store thermometers in a cool place and inside a building when not in use; do not leave a thermometer in a vehicle that could change in temperature to very hot or very cold, resulting in thermal shock to the thermometer.
  - — Check the batteries of thermistor-type thermometers for proper voltage before using.
  - — Record the calibration data in the log book for each thermometer—liquid-in-glass, thermistor thermometer, or thermistor-containing field-measurement instrument. Note if a thermometer has been serviced or replaced.

CALIBRATION 6.1.2

Thermometer calibration differs from the process by which a pH or conductivity sensor is adjusted until the accuracy of its performance conforms to that of an accepted calibration standard. For temperature measurements, calibration[2] refers to a comparison or accuracy check at specified temperatures against a thermometer that is certified by the National Institute of Standards and Technology (NIST), or is manufacturer-certified as NIST traceable. Calibration should be performed in a laboratory environment every 6 to 12 months, depending on the manufacturer's recommendation.

- **Field thermometers:** Only calibration thermometers having current NIST certification or traceability can be used for checking the accuracy of (calibrating) field thermometers.
  - — **In the case of continuous monitors,** a nonmercury calibration thermometer can be used in the field to check or monitor temperature readings whenever other field-measurement sensors are calibrated. See Wagner and others (2006) for specific guidelines for continuous monitors.
- **Calibration thermometers** are calibrated during their manufacture and certified as NIST-certified or NIST-traceable at the manufacturing laboratory. The USGS requires that calibration thermometers be recertified by a professional calibration service at least every 2 years, or be replaced with a calibration thermometer having current certification.
  - — Calibration thermometers should be reserved for calibration and should not be used routinely as field thermometers (see **TECHNICAL NOTE**). **Mercury-filled thermometers must never be used outside of the laboratory.**
  - — The thermistors included in other field-measurement instruments must be calibrated (checked) routinely, as specified below for thermistor thermometers, since accurate determination of other field measurements depends on the accuracy of temperature measurements. Thermistors that are incorporated into instruments designed to measure, for example, specific electrical conductance, dissolved oxygen, and pH commonly provide automatic temperature compensation.

[2]Calibrate: "To check, adjust, or systematically standardize the graduations of a quantitative measuring instrument" (American Heritage Dictionary, 1976).

— **All thermometers must be tagged with their most recent date and source of certification** (NIST-certified or -traceable source for calibration thermometers and office-laboratory source for field thermometers).

- **A log book is required** in which the calibration and certification history of each calibration and field thermometer is recorded.

TECHNICAL NOTE: The accuracy of a thermometer may vary over time, depending on factors such as the quality of its manufacture, the frequency of its use, and the conditions to which it is exposed. Shock, contamination, rapid heating and cooling, and mechanical stress are some factors that can affect the stability of a liquid-in-glass or thermistor thermometer (ICL Calibration Laboratories, 2003, 2005; ASTM International, 2005).

6.1.2.A CALIBRATION THERMOMETERS

Calibration thermometers (table 6.1-1) can be either a liquid-in-glass (mercury or spirit) or thermistor (digital) type thermometer, but must carry a current NIST certification or NIST-traceable certification that is no more than 2 years old. The actual duration of the calibration depends on the date of thermometer certification (not the date of purchase), how frequently the thermometer is used, and the conditions (thermal, chemical, and physical) to which it has been subjected during field operations and storage (see "Maintenance, cleaning, and storage" in section 6.1.1).

- **Check that the calibration thermometer has an NIST certification or traceable certificate that is within a 2-year period of original certification or recertification.**
- **Liquid-in-glass calibration thermometer:**
  - — Before each use, inspect the thermometer for cracks, internal condensation, and liquid separation; if any of these conditions are observed, the thermometer must be replaced.
  - — If the thermometer has been stored or used improperly, exposed at some length to sunlight or heat, or if its accuracy is otherwise in question, **check its readings at temperatures of approximately 0°, 25°, and 40°C, against those of another calibration thermometer that has been certified within the past 2 years.** If the environmental air or water temperatures to be measured fall below or exceed this range, add calibration points to bracket the anticipated temperature range.

- **Thermistor calibration thermometer:**
  - — Before each use, inspect the instrument (temperature sensor, digital display, wires or leads, and plugs) for signs of wear or damage; check that batteries are at full voltage.
  - — If the thermometer has been improperly stored or used, exposed at some length to sunlight or heat or extreme cold, or if its accuracy is otherwise in question, check its readings at five temperatures within the range of 0° to 40°C, against those of another currently certified calibration thermometer. If the environmental air or water temperatures to be measured fall below or exceed this range, add calibration points to bracket the anticipated temperature range.
- **Once NIST certification has expired** (exceeded the 2-year USGS limit):
  - — The thermometer either must be replaced with a currently certified thermometer or be recertified through a professional calibration service.[3] An office-laboratory calibration check does not constitute recertification of NIST traceability of a calibration thermometer.
  - — It is advisable to replace all mercury thermometers with a spirit or thermistor thermometer in order to avoid potential mercury contamination. The mercury thermometer must be disposed of in strict accordance with safety regulations.

Do not use calibration thermometers as routine field thermometers. Reserve their use for calibrating field thermometers.

FIELD THERMOMETERS 6.1.2.B

Field thermometers, whether of the liquid-in-glass or thermistor (digital) type, and whether or not they are themselves NIST-traceable,

[3]The cost of commercial calibration services can vary widely. Examples of laboratories that are accredited to perform thermometer calibrations and certification include: National Institute of Standards and Technology (http://ts.nist.gov/ts/htdocs/230/233/calibrations/); ICL Calibration Laboratories (www.icllabs.com); Lab Safety Supply, Inc. (https://www.labsafety.com/calibration). (URLs cited were accessed 11/28/2005).

require regular accuracy checks against a calibration thermometer. Carry an extra thermometer in the event that the accuracy of a field thermometer is in question. **Note, however, that field checking of a thermometer's accuracy does not substitute for the required annual laboratory calibration.**

- At a minimum, calibrate each field thermometer every 12 months—the time interval depends on the amount of use and abuse to which the thermometer has been subjected and on its manufacture. According to thermometer manufacturers, some models of thermistor thermometers require calibration every 6 months (YSI, 2005). Quarterly or possibly monthly calibration can be required if the thermometer is in heavy use; was exposed to thermal shock, an extended period of direct sunlight, or extreme shifts in temperature; or was exposed to aggressive chemical solutions. The calibration history from the log book can indicate the expected life of the thermometer.
- **Each thermometer that passes the accuracy check must be tagged with the date of calibration.** Thermometers that do not pass the accuracy check must be repaired, if possible, or else discarded or otherwise retired from use.
- The annual calibration of field thermometers can be performed in the office laboratory or by an NIST-accredited commercial laboratory. To calibrate a thermometer, check its readings across a range of temperatures as described below in the instructions for water-bath calibration procedures. Temperature checks must bracket and include points that represent the temperature range expected to be encountered in the field. **EXCEPTION:** Thermistors in continuous water-quality monitors can be field-checked annually (or more frequently, if necessary) with a nonmercury NIST-certified or NIST-traceable thermometer.
  - — Fully submerge the bulb and liquid column if using a total-immersion liquid-in-glass thermometer.
  - — Keep calibration and field temperature sensors (thermistor or liquid-in-glass type) submerged throughout the calibration process.
  - — Record thermometer readings throughout the bath warming and cooling periods and while keeping the water stirred or otherwise circulated (thermistor readings will be recorded with greater frequency).
  - — Check meter batteries periodically for proper voltage when using a thermistor-type thermometer.

— Record the calibration data in the instrument log book for each thermistor thermometer (including thermistor-containing field meters), noting if a temperature sensor has been replaced.

Calibrate field thermometers every 12 months.

To calibrate field thermometers when a commercial refrigerated water bath is available:

1. Precool the sensor of the thermometer(s) being tested (field thermometer) to 0°C by immersing it in a separate ice/water bath.
2. Immerse the field and calibration temperature sensors in the refrigerated bath with a water temperature of approximately 0°C.
3. Position the temperature sensor(s) so that they are properly immersed and so that the scales can be read. Stir the water bath and allow at least 2 minutes for the thermometer readings to stabilize.
4. Without removing the temperature sensor(s) from the refrigerated water bath, read the field thermometer(s) to the nearest graduation (0.1 or 0.5°C) and the calibration thermometer to the nearest 0.1°C.
   a. Take three readings within a 5-minute span for each field thermometer.
   b. Calculate the mean of the three temperature readings for each field thermometer and compare its mean value with the calibration thermometer.
   c. If a liquid-filled field thermometer is found to be within ±1 percent of full scale or ±0.5°C of the calibration thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
   d. If a field thermistor is found to be within ±0.2°C of the calibration thermometer, set it aside for calibration checks at higher temperatures.
5. Repeat steps 1–4 in 25°C and 40°C water. Keep the bath temperature constant. Check the thermistors at two or more additional intermediate temperatures (for example, 15°C and 30°C).
6. Tag acceptable thermometers as “office-laboratory certified” with calibration date and certifier’s initials.

To calibrate field thermometers when a commercial refrigerated water bath is not available:

A. For the 0°C calibration

1. Freeze several ice cube trays filled with deionized water.
2. Fill a 1,000-milliliter (mL) plastic beaker or Dewar flask three-fourths full of crushed, deionized ice. Add chilled, deionized water to the beaker. Place the beaker of ice/water mixture in a larger, insulated container or Dewar flask. Place the calibration thermometer into the ice/water mixture and make sure that the temperature is uniform at 0°C by stirring and checking at several locations within the bath.
3. Precool the sensor of the field thermometer(s) to 0°C by immersing in a separate ice/water bath.
4. Insert the field thermometer(s) into the ice/water mixture. Position the calibration and field thermometers so that they are properly immersed and so that the scales can be read. Periodically stir the ice/water mixture and allow at least 2 minutes for the thermometer readings to stabilize.
5. After the readings stabilize, compare the temperature of one field thermometer at a time with that of the calibration thermometer. Without removing the temperature sensor(s) from the test bath, read the field thermometer(s) to the nearest graduation (0.1 or 0.5°C) and the calibration thermometer to the nearest 0.1°C.
   a. Take three readings for each thermometer within a 5-minute span.
   b. Calculate the mean of the three temperature readings for each thermometer and compare its mean value with the calibration thermometer.
   c. If the field liquid-filled thermometer is found to be within ±1 percent of full scale or ±0.5°C of the calibration thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
   d. If the field thermistor is found to be within ±0.2°C of the calibration thermometer, set it aside for calibration checks at higher temperatures.

B. For the "room temperature" calibration (25°C)

1. Place a Dewar flask or container filled with about 1 gallon of water in a box filled with packing insulation. (A partially filled insulated ice chest can be used for multiparameter instruments.) Place the calibration container in an area of the room where the temperature is fairly constant (away from drafts, vents, windows, and harsh lights).
2. Properly immerse the calibration and field thermometer(s) in the water. Cover the container and allow the water bath and thermometers to equilibrate.
3. Stir the water and, using the calibration thermometer, check the bath for temperature uniformity. Repeat this every 2 hours. It may be necessary to let the bath equilibrate overnight.
4. Compare one field thermometer at a time against the calibration thermometer, following the procedures described above in step A5 for the 0°C calibration.

C. For each temperature that is greater than 25°C

1. Warm a beaker of 1,000 mL or more of water to the desired temperature (for example, 40°C) and place it on a magnetic stirrer plate.
2. Follow the procedures described above in step A5 for the 0°C calibration.

Tag acceptable field thermometers as "office-laboratory certified" with the calibration date and certifier's initials.

Corrections can be applied to measurements made with a thermometer that is within ±1 percent of full scale or ±0.5°C of the calibration thermometer. Corrections should be applied by using a calibration curve or table, which is plotted in the log book for the instrument. **Thermistors found to be out of calibration by more than 0.2°C must be returned to the manufacturer for repair or replacement.**

Remember to tag and date acceptable field thermometers after calibration.

6.1.3 MEASUREMENT

Air temperature, in addition to water temperature, should be measured and recorded whenever water-quality samples are collected. Water temperature must always be measured in situ and in a manner that ensures that the measurement accurately represents the intended sample conditions. Before measuring air or water temperature:

- Inspect the liquid-in-glass thermometer to be certain that the liquid column has not separated.
  - — Inspect the glass bulb to be sure it is clean.
  - — Inspect the protective case to be sure it is free of sand and debris.
- Check that batteries are fully charged for thermister thermometers or temperature sensors incorporated into other field meters.

6.1.3.A AIR

Measure air temperature using a dry, calibrated thermometer.

- Place or hang the thermometer about 5 feet above the ground in a shaded area that is protected from strong winds but open to air circulation. Avoid areas of possible radiant heat effects, such as metal walls, rock exposures, or sides of vehicles.
- Allow 3 to 5 minutes for the thermometer to equilibrate, then record the temperature and time of day.
- Measure the air temperature as close as possible to the time when the temperature of the water sample is measured.
- Report routine air temperature measurements to the nearest 0.5°C. If greater accuracy is required, use a thermistor thermometer that has been calibrated to the accuracy needed.

6.1.3.B SURFACE WATER

The reported surface-water temperature must be measured in situ—**do not measure temperature on subsamples** from a sample compositing device. Measure temperature in such a manner that the mean or median temperature at the time of observation is represented (consult NFM 6.0 and fig. 6.0–1). Record any deviation from this convention in the data base and report it with the published data.

To measure the temperature of surface water:

- Making a cross-sectional temperature profile first, to determine the temperature variability of the stream section, is recommended—a hand-held digital thermometer works best for this purpose.
- To determine which sampling method to use (NFM 6.0), examine the cross-sectional profile and consider study objectives.
- Measure temperature in those sections of the stream that represent most of the water flowing in a reach. Do not make temperature measurements in or directly below stream sections with turbulent flow or from the stream bank (unless this specifically represents the intended condition to be monitored).

1. Use either a liquid-in-glass thermometer or a thermistor thermometer tagged as "office-laboratory certified" and dated within the past 12 months.
2. Record on field forms the temperature variation from the cross-sectional profile, and the sampling method selected.
    - **Flowing, shallow stream—**wade to the location(s) where temperature is to be measured. To prevent erroneous readings caused by direct solar radiation, stand so that a shadow is cast on the site for temperature measurement.
    - **Stream too deep or swift to wade—**measure temperature by lowering from a bridge, cableway, or boat a thermistor thermometer attached to a weighted cable. Do not attach a weight directly onto the sensor or sensor cable.
    - **Still-water conditions—**measure temperature at multiple depths at several points in the cross section.

3. Immerse the sensor in the water to the correct depth and hold it there for no less than 60 seconds or according to the manufacturer's guidelines until the sensor equilibrates thermally. The sensor must be immersed properly while reading the temperature; this might require attaching the thermistor to a weighted cable.

> **TECHNICAL NOTE:** For in-situ measurement with liquid-filled, full-immersion thermometers—the water depth to which the thermometer is immersed must be no greater than twice the length of the liquid column of the thermometer in order to make an accurate measurement.

4. Read the temperature to the nearest 0.5°C for liquid-in-glass and 0.2°C for thermistor readings—**do not remove the sensor from the water.**
   - When using a liquid-in-glass thermometer, check the reading three times and record on field forms the median of these values.
   - When using a thermistor thermometer, wait until the readings stabilize to within 0.2°C, then record the median of approximately the last five values.
5. Remove the temperature sensor from the water, rinse it thoroughly with deionized water, blot it dry, and store it.
6. Record the stream temperature on field forms. Determine the values as follows:
   - **In still water—median** of three or more sequential values.
   - **For equal discharge increments (EDI)—mean** value of subsections measured (use median value if measuring one vertical at the centroid of flow).
   - **For equal width increments (EWI)—mean or median** value of subsections measured.

6.1.3.C GROUND WATER

Measurements of ground-water temperature must be made downhole or with a flowthrough system at the end of purging to ensure that the temperature measured accurately represents ambient aquifer water conditions (consult NFM 6.0 for guidance). **Do not report a temperature value measured from a bailed ground-water sample.**

To measure the temperature of ground water:

- ▶ Select either the downhole or flowthrough-chamber sampling system (see NFM 6.0, fig. 6.0–4) and record the method used.
- ▶ Measure temperature with a thermometer that has been office-laboratory certified within the past 12 months and within the temperature range to be encountered.

1. Prepare the instruments for either the downhole or the flowthrough-chamber system.
   - **Downhole system—**lower the sensor in the well to just below the pump intake (the intake location depends on the sampling objectives).
   - **Flowthrough-chamber system—**properly immerse the thermistor or liquid-in-glass thermometer in the chamber. Keep the pump tubing from the well to the chamber as short as possible, out of direct sunlight, and off the ground. Keep the chamber out of direct sunlight and wind.
2. Begin water withdrawal from the well. Allow the thermometer to equilibrate with ground-water temperature for no less than 60 seconds or in accordance with the manufacturer's guidelines; record the readings and time intervals throughout the period of purging.
3. Toward the end of purging, record five or more sequential measurements, spaced at increments of 3 to 5 minutes or more.
   - If the thermistor temperature is stable within the 0.2°C criterion, report the median of the final five measurements (table 6.0–1). (For a liquid-in-glass thermometer, there should be only slight fluctuation around 0.5°C.)
   - If the stability criterion has not been met, extend the purge time and consult the well-purging objectives of the study. Report the median of the last five (or more) sequential measurements and record any instability on field forms.
4. Remove the thermometer from the water, rinse it thoroughly with deionized water, blot it dry, and store it as described in 6.1.1.

6.1.4 TROUBLESHOOTING

Contact the instrument manufacturer if the suggestions on table 6.1-2 fail to resolve the problem, or if additional information is needed.

When using thermistor thermometers:

- Check the voltage of the batteries.
- Start with good batteries in instruments and carry spares.

Table 6.1–2. Troubleshooting guide for temperature measurement

Symptom	Possible cause and corrective action
Liquid-in-glass thermometer does not read accurately	• Check thermometer to see that the liquid is not separated—if separated, take back to the office laboratory to reunite column or for disposal.
Thermistor thermometer does not read accurately	• Dirty sensor—remove dirt and oil film. • Weak batteries—replace with new batteries.
Erratic thermistor thermometer readings	• Bad or dirty connection at meter or sensor—tighten or clean connections. • Break in the cables—replace cables. • Weak batteries—replace with new batteries.
Thermistor thermometer slow to stabilize	• Dirty sensor—clean sensor to remove dirt and oily film.

6.1.5 REPORTING

USGS temperature measurements should be stored in the National Water Information System (NWIS) data base. These data may be published electronically and (or) on paper as the verified negative or positive value measured, as described below.

- **Thermistor thermometer measurements:** Store manually recorded temperature measurements in the data base to the user-verified precision of the instrument (generally, 0.1 or 0.2°C, provided that the thermometer calibration verifies this accuracy). Electronically recorded temperature data may be stored unrounded. Unrounded temperature data in the database must be rounded when retrieved for publication.
- **Liquid-in-glass thermometer measurements:** Record temperature measurements in the data base to the nearest 0.5°C.
- Any values less than 0.1°C are highly questionable and should be published only after a complete calibration check of the equipment used.
- USGS field measurements of air and water temperature must be entered on the paper or electronic field form and stored in the NWIS data base.
  - — Be sure to store all data under the correct parameter and method (if available) codes.
  - — Store air and water temperature measurement data with replicate samples **only if replicate measurements were made.** Enter replicate measurements under the correct medium code for quality-control (QC) samples; alternatively, distinguish the replicate from the regular sample by using the unique time-of-sampling that was assigned to QC samples for that site and date.
  - — Do not store the regular-sample measurement data with the replicate-sample data. **Enter regular-sample data only once in the NWIS data base.**
- Record the accuracy range of the instrument in the data base, if possible. Report the accuracy range with the published values.

Report only those water temperature values that were measured in situ.

SELECTED REFERENCES

American Heritage Dictionary of the English Language, 1976, Calibrate: Boston, Houghton Mifflin Company, p. 190.

American Public Health Association, American Water Works Association, and Water Environment Federation, 2005, Standard methods for the examination of water and wastewater (21st ed.): Washington, D.C., American Public Health Association, p. 2-61 to 6-62.

ASTM International, 2005, Temperature measurement, *in* ASTM Book of Standards, v. 14.03, July 2005, accessed December 16, 2005, at http://www.techstreet.com/info/astm.tmpl.

Brooklyn Thermometer Company Inc., 2005, FAQ - How "accurate" is my thermometer?: accessed December 16, 2005, at http://www.brooklynthermometer.com/cgi-local/SoftCart.exe/online-store/scstore/sitepages/faq-2-4.html?L+scstore+ytma8290+1135558467#ques4.

Hem, J.D., 1989, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, p. 18.

ICL Calibration Laboratories, Inc., 2003, NIST GMP-11, Good measurement practice for assignment and adjustment of calibration intervals for laboratory standards, accessed December 16, 2005, at http://www.icllabs.com/pdfs/GMP%2011%20Mar%202003.pdf.

ICL Calibration Laboratories, Inc., 2005, accessed December 16, 2005, at http://www.icllabs.com/.

Lab Safety Supply, 2005, accessed December 16, 2005, at https://www.labsafety.com/calibration/.

Stevens, H.H., Jr., Ficke, J.F., and Smoot, G.F., 1975, Water temperature--influential factors, field measurement, and data presentation: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D1, 65 p.

Thermometrics, 2005, Thermometrics—What is a thermistor?: accessed December 16, 2005, at http://www.thermometrics.com/htmldocs/whatis.htm.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, available online at http://pubs.water.usgs.gov/twri9A.

Wagner, R.J., Boulger, R.W. Jr., Oblinger, C.J., and Smith, B.A., 2006, Guidelines and standard procedures for continuous water-quality monitors — station operation, record computation, and data reporting: U.S. Geological Survey Techniques and Methods, book 1, chap. D3.

Ween, Sidney, 1968, Care and use of liquid-in-glass laboratory thermometers: Transactions of Instrument Society of America, v. 7, no. 2, p. 93-100.

Wood, W.W., 1976, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, 24 p.

YSI, 2005, Temperature - FAQs - How do thermistors fail; what are typical failure modes for thermistors?, accessed December 16, 2005, at http://www.ysitemperature.com/med-faq.html#4.

ACKNOWLEDGMENTS

This National Field Manual responds to advances in technology and science and to the developing needs for water-quality monitoring. Its aim is to provide scientifically sound guidance to USGS personnel and to document USGS requirements for collecting water-quality data. As a result, the expertise of numerous scientists has been tapped in developing this manual and keeping it current. A great debt of gratitude is owed to the following original authors, editors, and reviewers of Chapter A6, Section 6.1 of this field manual: M.E. Brigham, E.A. Ciganovich, I.M. Collies, J.V. Davis, C.M. Eberle, R.J. Hoffman, R.T. Iwatsubo, J.K. Kurklin, R.J. LaCamera, V.W. Norman, C.E. Oberst, B.B. Palcsak, K.A. Pearsall, D.B. Radtke, F.C. Wells, Chester Zenone, and the analysts of the USGS National Water Quality Laboratory. Special appreciation is extended to our colleagues and collaborators from the Hach, In-Situ Inc., and YSI Inc. companies.

Improvements to the technical quality of this revision of Section 6.1, Temperature, can be attributed to the expertise and conscientious efforts of technical reviewers D.A. Evans, K.K. Fitzgerald, and S.C. Skrobialowski. The editorial and production quality of this report is a credit to I.M. Collies and L.J. Ulibarri.

Chlorophyll Collection and Processing for Fall Line Stations

- Standard collection procedures are followed, ensuring ample volume for sediment, nutrient, and chlorophyll samples. (approx. 5 liters sample needed)
- After drawing sediment sample, draw 500mL sample into amber bottle for chlorophyll filtration and set aside.
- Complete nutrient samples, raw and filtered.
- Assemble filter apparatus
    - Filter flask
    - Magnetic base and cup
    - Hand vacuum pump
- Apply filter to base, attach cup, moisten filter with DI
- Gently agitate sample
- Measure 100mL sample in graduated cylinder and pour into cup
- Add 10 drops (1mL) Magnesium Carbonate solution to sample cup
- Apply vacuum and filter sample (vacuum not to exceed 15 cm/Hg, 6 in/Hg)
- When sample is filtered, remove cup. Using forceps remove filter and fold in half with particulate material inside
- Place inside foil sheet
- Repeat filtration three times, placing all filters in same foil sheet and ensuring they are separated within
- Wrap in larger foil sheet and place label on foil ensuring the number of filters and volume filtered through each is noted on the label
- Place in whirl-pac or Ziploc and put on ice until delivery
- Clean all equipment with liquinox and rinse well with tap and DI

APPENDIX 5 -- Quality Assurance Project Plan: Enhanced sediment collection for improving continuous sediment simulations, December 2005

QUALITY ASSURANCE PROJECT PLAN

Enhanced Sediment Collection for Improving Continuous Sediment Simulations

Prepared By:

Douglas L Moyer
Kenneth E Hyer
US Geological Survey
Virginia Water Science Center
1730 E. Parham Road
Richmond, VA 23228

December 2005

TABLE OF CONTENTS

Introduction and Project Description

Elevated suspended sediment levels are causing an adverse impact on the living resources and associated aquatic habitat of streams, rivers, and estuaries. These elevated suspended sediment levels may impair the growth of aquatic vegetation through reduced light levels, bury filter feeding organisms, reduce the habitat available for macroinvertebrates, and contribute to decreased fish populations. These elevated sediment levels also may be playing an important role in the transport of particle-associated contaminants, such as phosphorus and bacteria (Christensen, 2001).

The Chesapeake Bay, the Nation's largest estuary, also has been degraded through water-quality problems, loss of habitat, and over-harvesting of living resources. Excess sediment is having an adverse effect on the living resources and associated habitat of the Chesapeake Bay and its watershed. Because of excess nutrient and sediment levels, the Chesapeake Bay was listed as an impaired water body in 2000 under the Clean Water Act. The Bay must meet regulatory water-quality standards by 2010, and the CBP needs information with which to evaluate current conditions and progress towards meeting sediment-reduction measures.

In most streams, the majority of suspended sediments are transported during storm-flow periods (Wolman and Miller, 1960), the very time when the fewest data are generally collected. Although manual sampling of suspended sediment concentrations will produce an accurate series of point-in-time measurements, robust extrapolation to the many unmeasured periods (especially high-flow periods) has proven difficult because of the inherently complex nature of suspended sediment transport. Suspended sediment transport during storm events is extremely variable and it is difficult to relate a unique concentration to a given stream discharge. In one study, Christensen and others (2002) identified that only 50% of their eight study stations actually had significant correlations between suspended sediment and stream discharge. With the current limitations for predicting suspended sediment levels, innovative approaches for generating detailed records of suspended sediment concentrations are needed.

One promising new technology for improved suspended sediment determination involves the continuous monitoring of turbidity as a surrogate for suspended sediment concentrations. Turbidity measurements are well correlated to suspended sediment concentrations because turbidity represents an optical measure of water clarity and it is the presence of suspended sediments that directly influences this measurement of clarity. Using turbidity values as a surrogate for calculating suspended sediment concentrations is not new, but until recently, technological limitations have made this approach largely unreasonable. As early as 1977, Walling described this surrogate approach using turbidity and demonstrated a sharp reduction in suspended sediment prediction error using a turbidity-sediment relationship relative to a discharge-sediment approach. In the earlier-mentioned study by Christensen and others (2002) that demonstrated poor correlation between suspended sediment concentrations and discharge, 100% of their research stations demonstrated significant correlations between suspended sediment concentrations and turbidity measurements. The development of continuous turbidity records to calculate suspended sediment concentrations is now inherently more feasible because of technical improvements to in-situ water-quality sensors and improved telecommunications. Continuous turbidity measurement has now become a more

common field approach because it provides significantly more detailed and more accurate information on suspended sediment concentrations and loadings than was previously possible (Christensen and others, 2000; Christensen, 2001).

Objectives

This project will address the following objectives:

(a) Evaluate the use of continuous turbidity sensors as a surrogate for predicting suspended sediment concentrations, and calculating suspended sediment loads;

(b) Compare turbidity-derived suspended sediment loadings to loadings generated through classical approaches that rely on a relationship between flow and sediment (the ESTIMATOR model, for example).

(c) Evaluate which approach provides the most detailed and accurate suspended sediment data that can be incorporated into the various water-quality models of the Chesapeake Bay Watershed;

(d) Determine whether the turbidity-sediment surrogate approach is sufficiently robust over time that it results in reduced water-quality monitoring costs.

Project Organization and Responsibility

Table 1. Project organization and responsibility

Personnel and Affiliation	Position	Responsibility	Contact
Doug Moyer, USGS	Hydrologist	Project Manager, Data analysis, Sample Collection	804-261-2634 dlmoyer@usgs.gov
Ken Hyer, USGS	Hydrologist	Project Manager, Data Analysis, Sample collection	804-261-2636 kenhyer@usgs.gov
Brian Hasty, USGS	Hydrologic Technician	Monitor Maintenance	Contact Project Managers
Amy Jensen, USGS	Hydrologic Technician	Discrete Water-Quality Sampling	Contact Project Managers

Study Design

Continuously monitoring turbidity probes will be installed at 3 of the River Input Monitoring (RIM) or Non-tidal Network Monitoring stations; these established stations are currently monitored by the USGS for the Chesapeake Bay Program, and comprise the 9 major non-tidal rivers that drain into the Chesapeake Bay. The most likely stations to be instrumented with continuous turbidity probes include the Potomac River, the Rappahannock River (USGS Station Number 01668000), and the James River

(02035000); the specific site for continuous monitoring in the Potomac River Basin has yet to be identified. These three basins have been selected for this study because they are all major sediment-contributors to the Bay. Intensive manual sediment monitoring also will be performed during a broad range of flow conditions (including low-flow, intermediate-flow, and storm-flow conditions) to provide up to 45 paired measurements of suspended sediment concentrations and associated turbidity values. The intensive sediment sampling must be performed over the entire range of hydrologic conditions (including extremely high flows) because it is during storm-flow periods that the majority of sediments are transported. All sediment samples will be collected following the standard USGS protocols for suspended sediment sampling and representative sampling (USGS, 1998).

Locating the turbidity monitors at existing RIM stations provides several direct benefits to the study. As the team that manages the RIM project for all Virginia stations, we will integrate the current proposed study into the existing RIM program. By doing this, the proposed study will benefit from the historical body of data that has been collected at these stations, and the existing understanding of these systems. Additionally, by co-locating the turbidity probes with an established RIM station, we can use the existing telemetry equipment to provide nearly free real-time transfer and internet display of the turbidity data. Lastly, ongoing sediment and nutrient sampling at the RIM stations will defray many of the costs that would have been associated with sampling and maintaining equipment at any other location. For example, many of the costs associated with travel, sampling, laboratory costs, and salary required by the proposed study will be paid for as part of the RIM project.

The following approach will be used at each monitoring station to calculate suspended sediment concentrations and loads on the basis of measured turbidity values:

- Continuously recording turbidity meters will be installed at each stream gage. The turbidity meter must be installed in a location within the cross section that is representative. Upon installation, the meter will be connected to telemetry equipment that communicates the sensor data back to a central office location. Through this telemetry, the data can be observed and reviewed in “real time”.
- During the first year of the study, manual samples will be collected over a large range of flow conditions and analyzed for suspended sediment concentrations.
- Site-specific regression equations will be developed to relate turbidity values and suspended sediment concentrations over this large range of flow conditions.
- The site-specific regression equations will be used to predict continuous suspended sediment concentrations from the continuous turbidity data. Using the unexplained variance from the regression equation we can quantify the uncertainty in the suspended sediment predictions.
- The continuous suspended sediment concentrations and the continuous discharge record will then be used to predict continuous sediment loadings from each river to the Chesapeake Bay. These predicted sediment loadings will be compared to sediment load estimates from other existing methods (e.g. ESTIMATOR). Differences between the methodologies will be documented and evaluated.

This approach is completely analogous to the standard methods for developing a continuous record of discharge in which stream stage (water level) is recorded over time, a rating curve is developed for the station, and the rating curve is then used to calculate

discharge from the stream stage. A one-year pilot deployment of a turbidity probe on the James River during 2004 demonstrates a statistically significant correlation ($p<0.01$) between turbidity and suspended sediment concentrations (Figure 1).

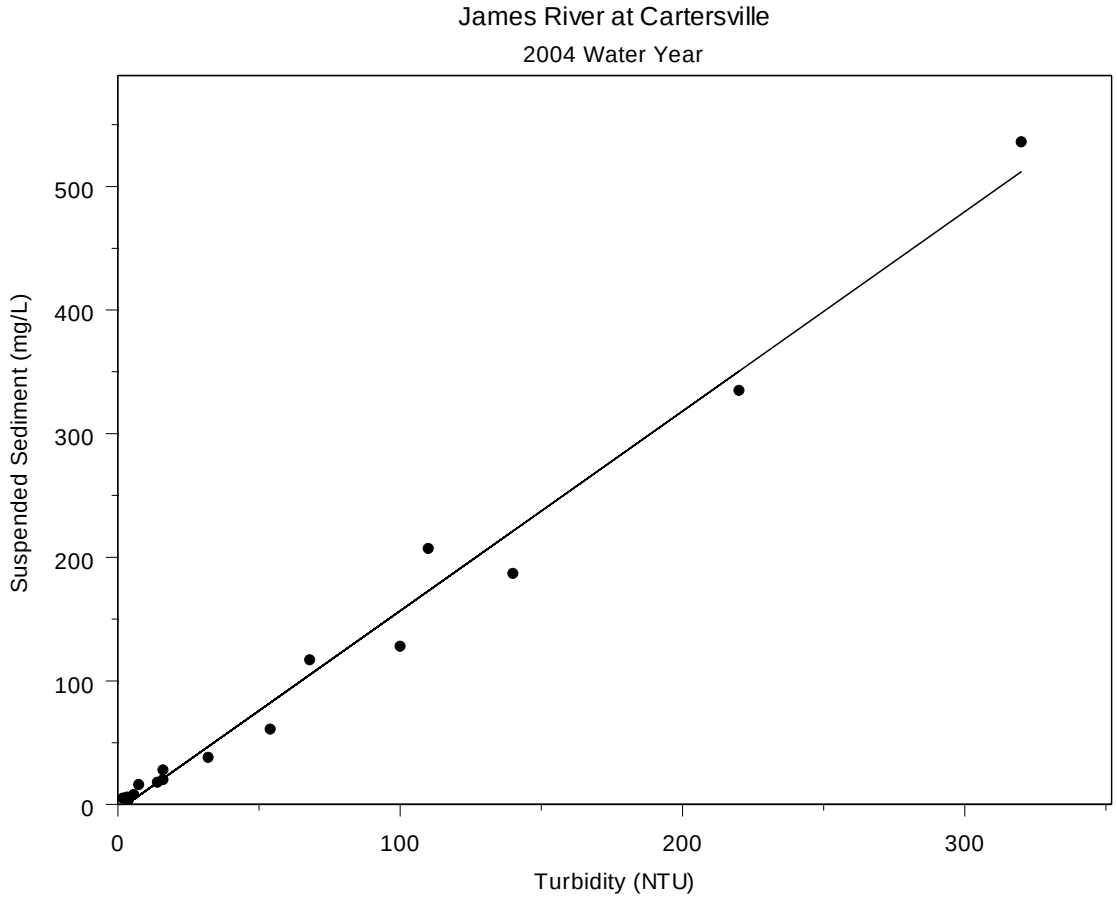


Figure 1. Relation between turbidity and suspended sediment on the James River at Cartersville, VA, 2004.

Continuous water-quality monitoring protocols

All continuous water-quality monitoring operations in the USGS are to be performed according to the USGS standard methods for the operation of this equipment. These standard operating procedures have been thoroughly documented by Wagner and others (2000) in their Water-Resources Investigations Report entitled: Guidelines and Standard Procedures For continuous Water-quality Monitors: Site Selection, Field Operation, Calibration, Record Computation, and Reporting. Because these published USGS Standard Operating Procedures (SOP) will be followed during this study, only a summary of these procedures will be outlined below and an internet link to the full SOP Manual is provided in the references section.

The continuous water-quality monitor (likely a YSI Model 6920 multi-parameter monitor) will be deployed at three of the existing River Input Monitoring Stations and configured to measure water temperature, turbidity, specific conductance, and pH at 15-minute intervals (this interval is commonly referred to as producing continuous data). The instrument will be connected to data logging and telemetry equipment that will

transfer all data to the USGS office in Richmond, VA, where the data will be displayed on the internet for access by all interested individuals. Following the initial deployment, approximately monthly maintenance visits will be performed on the continuous water-quality monitor to clean the equipment and check the calibration of the sensors. In-field recalibration will be performed during these monthly maintenance visits as necessary (following the equipment tolerances as specified by the monitor manufacturer and those outlined by Wagner and others, 2000). Following the monthly maintenance visit, the maintenance data will be used to determine whether the monitoring equipment was subject to bio-fouling or calibration drift. If either of these conditions were observed to be outside the SOP tolerances, the continuous water-quality record may be shifted to correct these data. At the conclusion of each water year, the data will be reviewed for accuracy, all shifts will be checked, the quality of the data will be rated (as excellent, good, fair, or poor), a station analysis for the water year will be prepared, and the finalized data will be published in the Annual Virginia Water Science Center Data Report. By following the standard procedures outlined by Wagner and others (2000), these continuous data will be of known quality and will be able to be compared to any other continuous water-quality data that also were collected following these guidelines.

Discrete water-quality sampling protocols

Discrete water-quality samples will be collected from each of the three continuous monitoring stations, over a wide range of flow conditions, as part of the ongoing River Input Monitoring Project. These discrete water-quality samples will be collected following standard USGS protocols for the collection of water-quality samples (USGS, 1998). As these standard methods are well documented in published USGS manuals, only a summary is presented here. Samples will be collected over a wide range of flow conditions, with special effort paid to the collection of water-quality samples during storm-flow conditions. Samples that are collected following USGS protocols will be analyzed using USGS-approved methods for the analysis of those samples. Suspended sediment samples will be shipped to the USGS Eastern Region Sediment Laboratory for analysis following approved sediment-analysis techniques (Sholar and Shreve, 1998). Remaining water-quality analyses will be submitted to the Virginia Division of Consolidated Laboratory Services (DCLS). This laboratory has been reviewed and approved by the USGS for the analyses that are performed. As described in the USGS manuals for water-quality sampling and analysis, approximately 10 percent of the samples will be made up of quality-control samples, such as blanks and duplicate samples. Additional detailed information regarding the laboratory methods and analyses performed by DCLS are available in the form of a RIM Project-specific QAPP that is submitted to the Chesapeake Bay Program annually.

During the collection of all water-quality samples, a project-specific field form will be used to document the specific environmental conditions under which each sample was collected. In the field, this form will be the responsibility of the lead technician collecting samples. Upon returning to the Virginia Water Science Center, the field form will be delivered to the Virginia Water Science Center Data Manager for entry into the USGS water-quality database. Standard data-flow practices within the Virginia Water Science Center have been documented in the Virginia Water Science Center's Quality

Assurance Plan for Water-quality Activities (USGS, 2003). This quality assurance plan documents the processing of all data collected within the office, including sample handling and tracking, data management, as well as data review and publication. Similar to the review of all continuous water-quality data at the end of a given water year, all discrete water-quality data will be reviewed at the end of the water year and published in the Annual Virginia Water Science Center Data Report after these data have been finalized and approved.

Data Analysis and Measures of Success:

Multiple-linear regression analyses will be used to develop statistically significant regressions between continuously measured turbidity and suspended sediment concentrations. Success will be measured through paired evaluations of the estimated sediment loadings to the Bay with (based on turbidity-sediment regressions) and without the enhanced data collection (ESTIMATOR approach). These data comparisons are expected to improve sediment loading estimates for the Bay. Additionally, this demonstration project should encourage the application of this technology at other existing RIM stations and other basins throughout the non-tidal portions of the Bay Watershed. Lastly, the project will provide refined estimates of suspended sediment loads and concentrations that can be used in existing and future sediment transport models.

Schedule

Table 2. Project schedule, based on USGS Fiscal Years

	FY06 (Months)												FY07 (Months)												FY08 (Months)											
	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Project planning meetings with stakeholders; application for necessary permits																																				
Order and install instrumentation and equipment																																				
Write / submit QA/QC plans																																				
Collect turbidity data and storm samples.																																				
Develop initial turbidity-sediment regression equations																																				
Verify turbidity-sediment regression equations through continued data collection																																				
Compare sediment loads – turbidity vs. ESTIMATOR																																				
Annual CIMS data delivery																																				
USGS interpretive report describing results (by June 2008)																																				

References

Christensen, V.G., Jian, Xiaodong, and Ziegler, A.C., 2000, Regression analysis and real-time water-quality monitoring to estimate constituent concentrations, loads, and yields in the Little Arkansas River, south-central Kansas, 1995-99: U.S. Geological Survey Water-Resources Investigations Report 00-4126, 36 p.

Christensen, V.G., 2001, Characterization of surface-water quality based on real-time monitoring and regression analysis, Quivira National Wildlife Refuge, south-central Kansas, December 1998 through June 2001: U.S. Geological Survey Water-Resources Investigations Report 01-4248, 28 p.

Christensen, V.G., Rasmussen, P.P., and Ziegler, A.C., 2002, Comparison of estimated sediment loads using continuous turbidity measurements and regression analysis [abst.], in Proceedings of Turbidity and Other Sediment Surrogates Workshop, April 30-May 2, 2002, Reno, NV.

Moyer, D. L., 2005, Quality Assurance Project Plan for the Virginia River Input Monitoring Plan. Available upon request to: dlmoyer@usgs.gov, or kenhyer@usgs.gov

Sholar, C.J., and Shreve, E.A., 1998. Quality-assurance plan for the analysis of fluvial sediment by the northeastern region, Kentucky District Sediment Laboratory. U.S. Geological Survey Open-File Report 98-384, 27p.

USGS, 1998, National Field Manual for the Collection of Water-Quality Data: Techniques of Water-Resources Investigations, Book 9, variously paginated. Available on the internet: http://water.usgs.gov/owq/FieldManual/index.html

USGS, 2003, Quality-Assurance Plan for Water-Quality Activities in the Virginia District. This QA Plan is electronically available at: http://va.water.usgs.gov/LOCAL/QW_QAplan_2003.pdf

Wagner, R.J., Mattraw, H.C., Ritz, G.F., and Smith, B.A., 2000, Guidelines and Standard Procedures For continuous Water-quality Monitors: Site Selection, Field Operation, Calibration, Record Computation, and Reporting. U.S. Geological Survey Water-Resources Investigations Report 00-4252. Available online at: http://pubs.usgs.gov/wri/wri004252/

Walling, D.E., 1977. Assessing the accuracy of suspended sediment rating curves for a small basin, Water Resources Research, 13:531-538.

Wolman, M.G., and Miller, J.P., 1960, Magnitude and frequency of forces in the geomorphic processes: Journal of Geology, v. 68 p.54-74.